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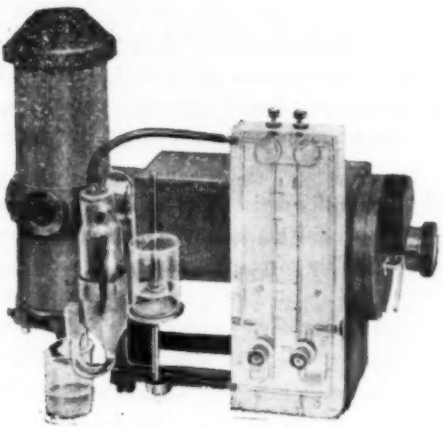

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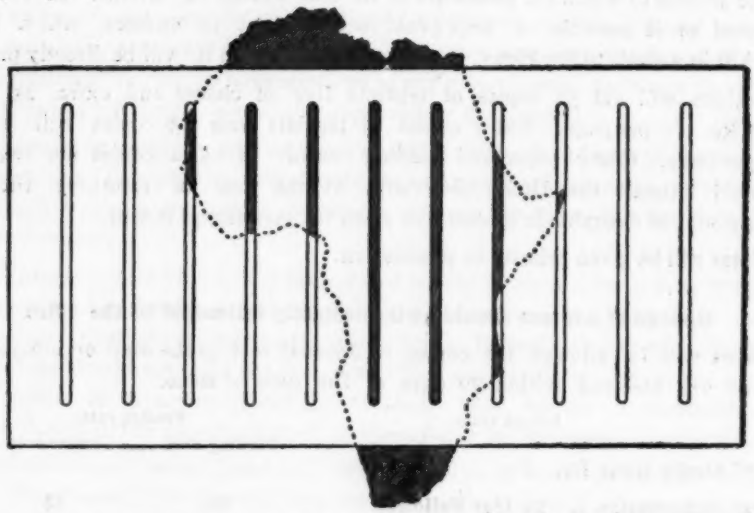

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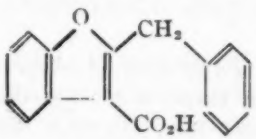
EXPERIMENTS ON THE SYNTHESES OF FURANO COMPOUNDS. PART XIV. ACYLATION OF 2- AND 3- SUBSTITUTED BENZOFURANS

By J. N. Chatterjea

Acylation of benzofurans, substituted by alkyl or aryl groups in 2- and 3-positions, has been examined and it is shown that the benzofurans, substituted in 2-position, are acylated in 3-position and *vice versa*. Formylation of 2-benzylcoumarone has given a formyl-β brazan. Alternative methods of synthesis of α- and β-brazans have been described.

Substitution reactions of benzofurans have been studied extensively by several workers (Stoermer *et al.*, *Ber.*, 1897, **30**, 2094; 1902, **35**, 1633; 1909, **42**, 199; *Annalen*, 1900, **312**, 237; Smith, *Chem. Abs.*, 1938, **32**, 2938; Adams and Rindfusz, *J. Amer. Chem. Soc.*, 1919, **41**, 648; Robertson *et al.*, *J. Chem. Soc.*, 1939, 921; 1938, 306; 1949, 2057 etc.) and an excellent summarised account may be found in "Heterocyclic Compounds" (Elderfield and Meyer, Vol. 2, p., 17, Wiley, New York). During the synthesis of various condensed benzofurans, it was intended to study the course of substitutions of benzofurans having alkyl or aryl groups in 2- and 3- positions and, for this purpose, studies on acylation of benzofurans by the Friedel-Crafts reaction (Smith, *loc. cit.*) or formylation by dimethylformamide were undertaken. This work was, however, anticipated by a recent publication of Buu-Hoï *et al.* (*J. Chem. Soc.*, 1955, 3688) and so the part of the results, not covered by these workers, is reported herein.

Acylation of 2-Substituted Benzofurans.—Acetylation of 2-methylcoumarone by acetyl chloride and stannic chloride afforded an excellent yield of 2-methyl-3-acetylcoumarone. The orientation was established by oxidising the product with sodium hypobromite to the known 2-methylcoumarone-3-carboxylic acid (cf. Part XII, this *Journal* 1957, **34**, 299). 2-Benzylcoumarone (Stoermer *et al.*, *Ber.*, 1924, **57**, 72) was similarly acylated in excellent yield to 3-acetyl-2-benzylcoumarone (Buu Hoï *et al.*, *J. Chem. Soc.*, 1955, 3693). This compound was orientated by oxidising it with sodium hypobromite to 2-benzylcoumarone-3-carboxylic acid (I) which was cyclised to 11-hydroxy-β-brazan and then converted into β-brazanquinone. 2-Phenylcoumarone (and its derivatives) was similarly converted into acetyl derivative and oriented.



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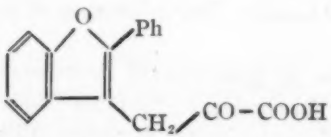
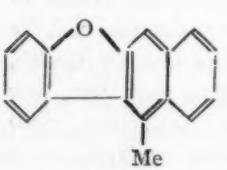


(II)

Formylation of 2-phenylcoumarone with dimethylformamide and phosphorus oxychloride gave an excellent yield of 3-formyl-2-phenylcoumarone, orientation of which was established by oxidising it with potassium permanganate in acetone to

2-phenylcoumarone-3-carboxylic acid (this *Journal*, 1956, **33**, 175, 447). The aldehyde was converted into the α-ketonic acid (II) *via* the corresponding azlactone and then into α-brazan by hydrobromic acid in acetic acid, the decarboxylation having taken place before cyclisation.

Formylation of 2-benzylcoumarone gave an unexpected result. An aldehyde was obtained in poor yield and analysed for $C_{17}H_{10}O_2$, indicating introduction of two formyl groups and elimination of a molecule of water. On oxidation this aldehyde gave an acid, $C_{17}H_{10}O_3$, which furnished β-brazan on decarboxylation. The aldehyde is therefore a formyl-β-brazan which itself could not be obtained on formylation of β-brazan. On reduction by the Wolff-Kishner method, the aldehyde was converted into a methyl-β-brazan, not identical with either of the known 7- or 10-methyl-β-brazan and also proved different from 2-, 8- and 9-methyl-β-brazans which were synthesised for the purpose. As this β-brazan does not afford the corresponding quinone on oxidation with chromic acid, it appears likely that the methyl group is at the 11- position. In an attempt to settle this orientation, the cyclodehydration of 3-acetyl-2-benzylcoumarone to 11-methyl-β-brazan (III) was tried by a variety of reagents, but to no success. The difficulty in cyclising 2-acetyl-3-benzylcoumarone may be recalled in this connection (Chatterjea and Roy, this *Journal*, 1957, **34**, 155).



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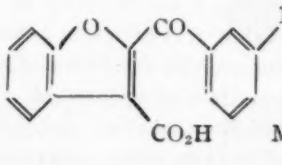

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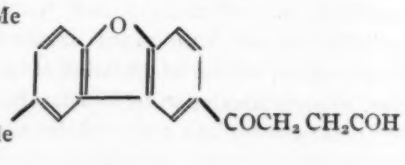
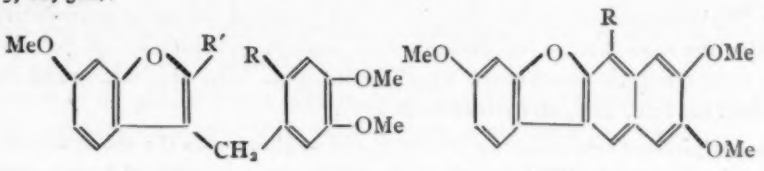


(V)

The synthesis of the above mentioned 9-methyl compound was carried out from 2-*p*-toluoylcoumarone-3-carboxylic acid by ring-closure to 9-methyl-β-brazanquinone followed by reduction (cf. Chatterjea, *ibid.*, 1944, **31**, 101). The cyclisation of 2-*m*-toluoylcoumarone-3-carboxylic acid (IV) afforded a mixture of 8- and 10-methyl-β-brazanquinones which were collectively reduced and then separated into 8-methyl- and the known 10-methyl-β-brazan. 2-Methyl-β-brazan was prepared from 2-methyldibenzofuran which on succinoylation gave a mixture of γ-ketonic acids of which the preponderating isomer must be (V). This was followed by reduction to the corresponding butyric acid, cyclisation, reduction of the resulting ketone, dehydration and dehydrogenation to 2-methyl-β-brazan. The orientation of the methyl group in this compound is open to question.

Acylation of 3-Substituted Benzofurans.—The formylation of 3-benzylcoumarone with dimethylformamide, on the other hand, gave an excellent yield of the difficultly accessible 2-formyl-3-benzylcoumarone (Chatterjea and Roy, *loc. cit.*). Similarly, 6-methoxy-3-benzyl- and 6-methoxy-3-(3 : 4-dimethoxybenzyl)- coumarone gave excellent yields of the corresponding 2-formyl derivatives. In the like manner, the Friedel-Crafts acylation of 6-methoxy-3-(3 : 4-dimethoxybenzyl)-coumarone with acetyl, phenylacetyl, propionyl or benzoyl chloride afforded the corresponding 2-acyl derivatives which were valuable intermediates in β-brazan synthesis (Chatterjea, this *Journal*, 1953, **30**, 1).

During this work, experiments have been carried out towards the synthesis of 3-(2′-acylbenzyl)-coumarones of the type (VI : R = acyl ; R′ = H) so as to prepare 6-alkyl derivatives of β-brazan (VII) on cyclodehydration and also with the object of synthesising ψ-trimethylbrazilone (VI : R′ = H; R = COOH) (Perkin and Robinson, *J. Chem. Soc.*, 1909, **95**, 381).



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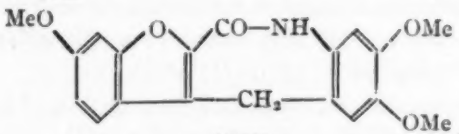

(VIII)

For this purpose, the acid (VI : R = H ; R′ = COOH) was esterified with diazomethane and then nitrated with nitric acid in acetic acid to the nitro-ester (VI : R = NO_2 ; R′ = COOMe) and then hydrolysed to the corresponding acid. The orientation of the nitro group was established by reducing the nitro-acid to the corresponding amino-acid with ferrous sulphate and ammonia and then cyclised to the lactam (VIII) on treatment with acetic anhydride. The nitro-acid (VI : R = NO_2; R′ = COOH) was decarboxylated by copper-bronze in quinoline, and the product reduced by stannous chloride to the corresponding amine (VI : R = NH_2 ; R′ = H), isolated as the hydrochloride. The conversion $NH_2 \rightarrow CN \rightarrow COOH$ did not proceed satisfactorily with this amine, the diazotisation step being cumbersome. Although traces of acidic material (too meagre to permit isolation) obtained from the crude cyano compound presumably contain (VI : R = COOH ; R′ = H), it is clear that the above route is inefficient and warrants further investigation. A more fruitful result was, however, obtained when the Friedel-Crafts acylation of (VI : R = H; R′ = COOMe) was done with acetyl chloride (or propionyl chloride) and the crude ester hydrolysed to (VI : R = COMe or COEt; R′ = COOH) whose thermal decarboxylation was attended with cyclisation, yielding the β-brazan (VII : R = Me or Et) directly.

*Experimental

3-Acetyl-2-methylcoumarone.—A mixture of 1-methylcoumarone (1.4 g., Adams and Rindfusz, *loc. cit.*) and acetyl chloride (0.8 g.) in pure dry carbon disulphide (10 c.c.) was treated at about 0° with stannic chloride (2.6 g.). Gradually a pink solid complex appeared. After leaving for 3 hours at the room temperature, the complex was decomposed with iced HCl and extracted with ether. The *ketone* distilled at 120-22°/3.3 mm and solidified to a colorless lump, m.p. 52° from petroleum ether and imparted an orange colour to H_2SO_4. (Found : C, 76.0 ; H, 5.9. $C_{11}H_{10}O_2$ requires C, 75.9; H, 5.8%).

* All m.p.s are uncorrected.

The 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in orange needles, m.p. 253-54°. (Found : N, 16.0. $C_{17}H_{14}O_5N_4$ requires N, 15.8%).

The *oxime* crystallised from methyl alcohol in colorless plates, m.p. 96°. (Found : C, 70.3; H, 5.6. $C_{11}H_{11}O_2N$ requires C, 69.8; H, 5.8%).

2-*Methylcoumarone-3-carboxylic acid* was obtained in nearly quantitative yield by oxidising the above ketone (in dioxan) with sodium hypobromite at 70° for 1 hour. After destroying the unchanged hypobromite with SO_2, the mixture on acidification furnished the acid, m.p. and mixed m.p. 191°.

3-*Acetyl-2-benzylcoumarone* was prepared as above with the aid of stannic chloride. The hard complex was decomposed with water-ether, the ethereal layer washed and distilled. The acetyl compound was obtained as a yellowish viscous liquid, b.p. 190°/2 mm. (Buu Hoï *et al.*, *J. Chem. Soc.*, 1955, 3693 record b. p. 229-30°/18 mm). (Found : C, 81.9 ; H, 5.7. Calc. for $C_{17}H_{14}O_2$: C, 81.7; H, 5.6%).

The 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in orange-red plates, m.p. 167°. (Found : N, 12.8. $C_{23}H_{18}O_5N_4$ requires N, 13.0%).

On oxidation with sodium hypobromite at 70° in dioxan solution for 1½ hours, 2-*benzylcoumarone-3-carboxylic acid* was obtained (yield 20-25%) which crystallised from acetic acid in prisms, m.p. 188°. (Found : C, 75.5 ; H, 4.5. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.8%). The compound imparted a violet-pink colour to H_2SO_4.

Cyclisation of 2-Benzylcoumarone-3-carboxylic Acid.—The acid (0.2 g.) was converted into the acid chloride by boiling with thionyl chloride (1 c.c.) in presence of a trace of pyridine for 1 hour. After removing thionyl chloride, the oily acid chloride was dissolved in pure CS_2 (3 c.c.), cooled and treated with $AlCl_3$ (0.6 g.) and left overnight. The aluminium complex was decomposed with iced HCl and the product (contaminated with sulphur compounds), which dissolved in alkali with violet fluorescence, was converted into β-brazanquinone, m.p. and mixed m.p. 245°, by oxidising the crude product with chromic acid (0.3 g.) in acetic acid (2 c.c.) for 2 minutes. (Found : C, 77.3; H, 3.3. Calc. for $C_{16}H_8O_3$: C, 77.4 ; H, 3.2%).

3-*Acetyl-2-phenylcoumarone* was prepared from 2 phenylcoumarone as above. The ketone, obtained as an oil, was identified by its 2 : 4-dinitrophenylhydrazone, m.p. 210°, undepressed on admixture with an authentic specimen (Chatterjea, this *Journal*, 1956, **33**, 175).

The 2 : 4-*dinitrophenylhydrazone* of 3-acetyl-2-*p*-chlorophenylcoumarone (Chatterjea and Roy, this *Journal*, 1957, **34**, 98), prepared similarly, crystallised from acetic acid in red plates, m.p. 210-11°. (Found : N, 12.6. $C_{22}H_{13}O_5N_4Cl$ requires N, 12.4%).

The 2 : 4-*dinitrophenylhydrazone* of 3-acetyl-2-*p*-tolylcoumarone (Chatterjea and Roy, *loc. cit.*) crystallised from acetic acid in orange leaflets, m.p. 209°. (Found : N, 12.8. $C_{23}H_{18}O_5N_4$ requires N, 13.0%).

3-*Formyl-2-phenylcoumarone.*—A mixture of 2-phenylcoumarone (1.0 g.), dimethylformamide (0.45 g.) and $POCl_3$ (0.9 g.) was heated on a boiling water-bath for 8 hours and then the mixture was cooled and carefully decomposed with alkali. The *aldehyde* separated as a colorless oil which solidified immediately (1.0 g.) and obtained

in prismatic needles from dilute alcohol, m.p. 74-75°. (Found: C, 81.3; H, 4.4. $C_{15}H_{10}O_2$ requires C, 81.1; H, 4.5%). The compound is fairly soluble in alcohol and develops a greenish yellow coloration with H_2SO_4. The *2:4-dinitrophenylhydrazone* crystallised from a large volume of acetic acid in orange-red leaflets, m.p. 285° (decomp.). (Found: N, 14.3. $C_{21}H_{14}O_5N_4$ requires N, 13.9%). The *oxime*, prepared in pyridine, was obtained in colorless crystalline mass from dilute alcohol, m.p. 144-45°. (Found: N, 5.6. $C_{15}H_{11}O_2N$ requires N, 5.9%).

Oxidation of the aldehyde with $KMnO_4$ in acetone at 45° afforded a small yield of 2-phenylcoumarone-3-carboxylic acid, identical with an authentic specimen.

Dehydration of the above mentioned oxime (0.3 g.) by boiling with acetic anhydride (3 c.c.) for 3 hours gave a small yield of 3-cyano-2-phenylcoumarone, m.p. and mixed m.p. 80-82°. (Found: N, 6.4. Calc. for $C_{15}H_9ON$: N, 6.4%).

α-Brazan from 3-formyl-2-phenylcoumarone.—A mixture of the aldehyde (2.2 g.), hippuric acid (2 g.), sodium acetate (1.0 g.) and acetic anhydride (21 c.c.) was heated on the water-bath for 1 hour. The *azlactone* gradually separated in yellow needles. Alcohol (40 c.c., 50%) was added to the mixture; the product (1.8 g.) was collected and crystallised from benzene in bright yellow plates, m.p. 225-26°. (Found: N, 3.8. $C_{24}H_{15}O_3N$ requires N, 3.8%).

Hydrolysis.—The azlactone (1.5 g.) was boiled with a mixture of sodium hydroxide (20 c.c., 10%) and alcohol (6 c.c.) for 24 hours. The mixture was diluted with water (15 c.c.), saturated with SO_2 and *2-phenylcoumarone-3-pyruvic acid* (II) isolated in the usual way and obtained in yellowish prisms from acetic acid, m.p. 170°. (Found: C, 72.8; H, 4.6. $C_{17}H_{12}O_4$ requires C, 72.9; H, 4.3%). The compound develops a greenish colour with alcoholic ferric chloride. On oxidation with alkaline hydrogen peroxide at 5°, this pyruvic acid gave a good yield of 2-phenylcoumarone-3-acetic acid, m.p. and mixed m.p. 142°. (Found: C, 76.1; H, 4.7. Calc. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8%).

Cyclisation.—A mixture of the above pyruvic acid (0.2 g.), acetic acid (3 c.c.) and hydrobromic acid (2 c.c., 48%) was boiled under reflux for 5 hours. The changes in colour of the mixture was: pink → light blue → bluish green → brown → pinkish brown. The oil that separated was taken up in ether after dilution and distilled in vacuum. α-Brazan quickly solidified and obtained in prismatic needles, m.p. and mixed m.p. 103°. (Found: C, 87.7; H, 4.7. Calc. for $C_{16}H_{10}O$: C, 88.1; H, 4.6%).

Formylation of 2-Benzylcoumarone.—A mixture of 2-benzylcoumarone (7 g.), dimethylformamide (5 g.) and $POCl_3$ (8 g.) was heated on the water-bath for 10 hours. In the beginning there were two layers but after a few hours the mixture became homogeneous. The whole was cooled, made strongly alkaline, extracted with ether and distilled. After a fore-run of unchanged material (b.p. 140°/0.3 mm) the residual dark high-boiling material was dissolved in alcohol and left in the refrigerator. Formyl-β-brazan was obtained as cream-coloured needles (0.6 g.), m.p. 167°, developing orange coloration with H_2SO_4. (Found: C, 82.6; H, 4.4. $C_{17}H_{12}O_2$ requires C, 82.9; H, 4.1%). The *oxime*, prepared in pyridine, crystallised from alcohol in colorless prisms,

m.p. 232°. (Found: C, 78.3; H, 4.6. $C_{17}H_{11}O_2N$ requires C, 78.2; H, 4.2%). The 2:4-*dinitrophenylhydrazone* crystallised from acetic acid in orange needles, m.p. > 290°. (Found: N, 14.0. $C_{23}H_{14}O_5N_4$ requires N, 13.1%).

On oxidation with a solution of potassium permanganate (0.3 g.) in water (4 c.c.) at 40°, this aldehyde (0.1 g.) furnished, in the usual way, the corresponding *carboxylic acid*, m.p. 260°, developing a yellowish colour with H_2SO_4. (Found: C, 77.1; H, 4.0. $C_{17}H_{10}O_3$ requires C, 77.8; H, 3.8%). On distillation with lime, this acid gave β-brazan in a pure condition, m.p. and mixed m.p. 207°.

Reduction of the Aldehyde.—A mixture of the aldehyde (0.5 g.), hydrazine hydrate (1 c.c., 80%) and diethyleneglycol (5 c.c.) was boiled under reflux for 3 hours, cooled, potassium hydroxide (1 g.) added and water removed from the system by distillation. The temperature of the mixture was raised to 210° and kept at this temperature for 3 hours. The *methyl-β-brazan* was isolated with ether and obtained in colorless needles from alcohol (0.35 g.), m.p. 91°; mixed m.p. with 10-methyl-β-brazan (m.p. 91°) was 65-70°. (Found: C, 87.5; H, 5.3. $C_{17}H_{12}O$ requires C, 87.9; H, 5.2%). The compound developed a yellow coloration with H_2SO_4, turning greenish on keeping. The *picrate*, prepared in alcohol, crystallised from alcohol, containing picric acid, in orange needles, m.p. 92° (with previous sintering). (Found: N, 9.7. $C_{17}H_{12}O.C_6H_3O_7N_3$ requires N, 9.1 %).

9-*Methyl-β-brazan.*—Coumaran-dione (0.75 g.) was condensed with *p*-methylphenacyl bromide (1.1 g.) in alcoholic sodium ethoxide (sodium 0.12 g. and alcohol 12 c.c.). The resulting *ethyl* 2-p-*toluoylcoumarone*-3-*carboxylate* (0.7 g.) was obtained in colorless prisms or plates, m.p. 144° from alcohol. (Found: C, 74.1; H, 5.3. $C_{19}H_{16}O_4$ requires C, 74.0; H, 5.2%). The compound showed an orange colour with H_2SO_4. On hydrolysis with aqueous alcoholic sodium hydroxide, p-*toluoylcoumarone*-3-*carboxylic acid* was obtained (purified through the crystalline sodium salt), crystallising from benzene-petroleum ether in colorless prisms, m.p. 150°. (Found: C, 72.8; H, 4.5. $C_{17}H_{12}O_4$ requires C, 72.9; H, 4.3%). On cyclisation through the acid chloride in the usual manner (this *Journal*, 1954, **32**, 101), 9-*methyl-β-brazanquinone* was obtained (yield 90%), crystallising from acetic acid in orange needles, m.p. 225°. (Found: C, 77.6; H, 3.7. $C_{17}H_{10}O_3$ requires C, 77.8; H, 3.8 %). On boiling for 5 hours with hydriodic acid, this quinone gave 9-*methyl-β-brazan*, crystallising from benzene-alcohol in colorless plates, m.p. 180-81°. (Found: C, 87.5; H, 5.3. $C_{17}H_{12}O$ requires C, 87.9; H, 5.2 %).

8-*Methyl-β-brazan.*—*m*-Methylacetophenone was prepared from *m*-toluic acid by interaction of the acid chloride with magnesiummalonic ester (Walker and Hauser, *J. Amer. Chem. Soc.*, 1946, **68**, 1386), yield 60%. Bromination of the ketone in chloroform solution gave a quantitative yield of *m*-methylphenacyl bromide, b.p. 120-22°/1.5 mm. (Found: Br, 36.8. Calc. for C_9H_9OBr: Br, 37.6%). On interaction with coumaran-dione in the usual way, *ethyl* m-*toluoylcoumarone*-3-*carboxylate* was obtained, crystallising from alcohol in prisms, m.p. 103°, which on hydrolysis gave th corresponding *acid*, crystallising from benzene-petroleum ether in prismatic needles, m.p 123-24°. (Found: C, 72.8; H, 4.5. $C_{17}H_{12}O_4$ requires C, 72.9; H, 4.3%).

On cyclisation through the acid chloride, a mixture of isomeric brazanquinones, m.p. 190-220°, was obtained in good yield. The mixture was then reduced with boiling hydriodic acid for 4 hours, when a mixture of 8- and 10-methyl-β-brazans was obtained. The mixture was separated fractionally from alcohol, when the less soluble 8-methyl-β-brazan was obtained as colorless plates, m.p. 207-208°. (Found : C, 87.4 ; H, 5.4. $C_{17}H_{12}O$ requires C, 87.9; H, 5.2 %). The mother-liquor on working up gave 10-methyl-β-brazan as colorless plates, m.p. and mixed m.p. 89-92°.

2-Methyl-β-brazan.—Dibenzofuran was recovered unchanged on attempted formylation with dimethylformamide. On formylation with zinc cyanide and hydrogen chloride (Adams *et al.*, *J. Amer. Chem. Soc.*, 1923, **45**, 2373; 1924, **46**, 1518) a moderate yield of 2-formyldibenzofuran (*J. Chem. Soc.*, 1937, 779) was obtained.

A solution of the formyl compound (6 g.) and hydrazine hydrate (3 c.c., 90%) in diethyleneglycol (30 c.c.) was boiled and then KOH (4.0 g.) was added ; the mixture was refluxed for 4 hours with the removal of water and the reduced material. The distillate and the residue were extracted with ether after dilution, dried, solvent removed and 2-methyldibenzofuran distilled. The compound was obtained as a colorless liquid (1.7 g.), b.p. 215°/80 mm, which solidified, m.p. 45° (Mayer and Krieger, *Ber.*, 1922, **55**, 1695, reported b.p. 215°/0.9 mm and m.p. 45°).

A mixture of 2-methyldibenzofuran (1.5 g.), tetrachloroethane (8 c.c.), nitrobenzene (2 c.c.) and succinic anhydride (1.3 g.) was cooled to 0° and anhydrous aluminium chloride (2 g.) was added with constant shaking. The brownish solution was left in the refrigerator for 3 days and then carefully decomposed with iced hydrochloric acid. Solvent was then removed in a current of steam and the residue on boiling with a mixture of acetic acid and ethyl acetate gave a crystalline mass (1.3 g.), m.p. 155° (clearing at 180°). This was fractionally crystallised from acetic acid when two products were obtained : (*i*) Compound, m.p. 236-37° (1.0 g.), presumably β-[8-(2-methyldibenzofuroyl)]-propionic acid (V). (Found : C, 72.0; H, 5.3. $C_{17}H_{14}O_4$ requires C, 72.4; H, 5.0 %). (*ii*) Compound, m.p. 159-60° (0.15 g.), probably β-[3-(2-methyldibenzofuroyl)]-propionic acid. (Found : C, 72.1 ; H, 5.1. $C_{17}H_{14}O_4$ requires C, 72.4 ; H, 5.0 %).

The ketonic acid (V) on reduction by Huang-Minlon's method, afforded the corresponding *butyric acid* which crystallised from benzene-petroleum ether in colorless prisms, m.p. 79-80°. (Found : C, 76.0 ; H, 6.2. $C_{17}H_{16}O_3$ requires C, 76.1 ; H, 6.0 %).

Cyclisation.—The butyric acid (0.3 g.) was dissolved in sulphuric acid (10 c.c., 90%) at the room temperature and after 12 minutes the mixture poured into water, extracted with ether, washed with alkali and the solvent evaporated, affording *2-methyl-7-keto-7 : 8 : 9 : 10-tetrahydro-β-brazan* which crystallised from alcohol in thick plates, m.p. 159°. (Found : C, 81.3 ; H, 5.8. $C_{17}H_{14}O_2$ requires C, 81.6 ; H, 5.6 %). The *oxime* crystallised from alcohol in cream-coloured plates, m. p. 257-58° (decomp.). (Found : N, 5.1. $C_{17}H_{15}O_2N$ requires N, 5.3 %).

The above ketone (0.1 g.) was reduced with lithium aluminium hydride (30 mg.) in ether (6 c.c.) at the room temperature for 20 minutes and then worked up to provide a crystalline carbinol which was mixed with palladised charcoal (20 mg.) and heated in a metal bath at 280°-300° for 2 hours. On working up, *2-methyl-β-brazan* was obtained

which crystallised from alcohol in colorless plates, m.p. 160°. (Found: C, 87.5; H, 5.3. $C_{17}H_{12}O$ requires C, 87.9; H, 5.2 %).

Formylation of 3-Benzylcoumarone.—Molecular quantities of the coumarone, dimethylformamide and phosphorus oxychloride were heated on the water-bath for 7 hours, left overnight and worked up as usual to furnish the 2-formyl derivative as a yellowish liquid (yield of the crude product, 90%). The 2:4-*dinitrophenylhydrazone* crystallised from acetic acid in orange-red needles, m.p. 244-46°, undepressed on admixture with an authentic specimen (Chatterjea and Roy, *loc.cit.*, p. 155). (Found: N, 13.8. Calc. for $C_{22}H_{16}O_5N_4$: N, 13.5 %).

2-Formyl-3-benzyl-6-methoxycoumarone.—6-Methoxy-3-benzylcoumarone on formylation with dimethylformamide for 2½ hours gave the 2-formyl derivative in quantitative yield. The product crystallised from alcohol in colorless needles, m.p. and mixed m.p. 107°.

2-Acetyl-3-benzyl-6-methoxycoumarone.—6-Methoxy-3-benzylcoumarone was acetylated in the cold as before with acetyl chloride and stannic chloride. The crude *ketone*, obtained as a semi-solid mass, gave a crystalline 2:4-*dinitrophenylhydrazone*, crystallising from acetic acid in orange-red leaflets, m.p. 245°. (Found: N, 12.0. $C_{24}H_{20}O_6N_4$ requires N, 12.2 %).

2-Formyl-3-(3:4-dimethoxybenzyl)-6-methoxycoumarone.—Equimolecular quantities of 6-methoxy-3-(3:4-dimethoxybenzyl)-coumarone, dimethylformamide and phosphorus oxychloride were heated on the water-bath for 1 hour. The mixture was cooled, decomposed with water and warmed with an excess of 10% alkali. The crystalline product (yield 85%) was recrystallised from alcohol and obtained in colorless needles, m.p. and mixed m.p. 137°.

2-Acetyl-3-(3:4-dimethoxybenzyl)-6-methoxycoumarone.—6-Methoxy-3-(3:4-dimethoxybenzyl)-coumarone was acetylated in carbon disulphide solution with equimolecular quantities of acetyl chloride and stannic chloride at 0°. The dark green complex was decomposed after 3 hours and the acetyl derivative isolated in quantitative yield, m.p. and mixed m.p. 155-56°. (Found: C, 70.4; H, 6.2. Calc. for $C_{20}H_{20}O_5$: C, 70.6; H, 5.9%). Similarly, by employing propionyl chloride, a moderate yield of 2-propionyl-3-(3:4-dimethoxybenzyl)-6-methoxycoumarone, m.p. and mixed m.p. 170°, was obtained.

2-Benzoyl-3-(3:4-dimethoxybenzyl)-6-methoxycoumarone was similarly prepared as above and obtained in colorless plates, m.p. 156° after crystallisation from alcohol and then acetic acid. (Found: C, 74.1; H, 5.3. $C_{25}H_{22}O_5$ requires C, 74.6; H, 5.5 %). The compound developed a yellow coloration with sulphuric acid. The *2-phenylacetyl* derivative was obtained in poor yield and crystallised from alcohol in a crystalline mass, m.p. 214° (with prolonged sintering). (Found: C, 75.0; H, 5.3. $C_{26}H_{24}O_5$ requires C, 75.0; H, 5.8 %).

Methyl 6-methoxy-3-(3:4-dimethoxybenzyl)-coumarone-2-carboxylate was prepared in a quantitative yield from the corresponding acid by esterifying an ethereal suspension of the acid with excess of diazomethane. The ester crystallised from alcohol in colorless prisms, m.p. 142.5-143°. (Found: C, 67.5; H, 5.6. $C_{20}H_{20}O_6$ requires C, 67.4; H, 5.6 %).

Methyl 6-Methoxy-3-(6-nitro-3 : 4-dimethoxybenzyl)-coumarone-2-carboxylate.—The foregoing ester (0.5 g.) was dissolved in acetic acid (15 c.c.) and treated with concentrated nitric acid (0.6 c.c.) at the room temperature. The solution turned slightly yellow and soon pale yellow crystals of the *nitro* compound (0.5 g.) began to separate. Crystallised from acetic acid, the nitro compound was obtained in nearly colorless needles, m.p. 205°. (Found : C, 60.0 ; H, 5.1 ; N, 3.8. $C_{20}H_{19}O_8N$ requires C, 59.9 ; H, 4.7 ; N, 3.5 %).

Hydrolysis.—The ester was hydrolysed by boiling an alcoholic suspension with sodium hydroxide solution (5%) till complete solution (10 minutes). After removing alcohol, the mixture was diluted with water, acidified and the pale yellow crystalline mass (yield 70%) recrystallised from acetic acid and obtained in micro-crystalline powder, m.p. 247° (decomp.). (Found : N, 5.0. $C_{19}H_{17}O_7N$ requires N, 4.8 %).

Decarboxylation.—The above nitro-acid (4 g.) was boiled with a mixture of quinoline (25 c.c.) and copper-bronze (1 g.) for 10 minutes. The mixture was cooled, acidified, extracted with ether and the ether solution washed with dilute alkali. *6-Methoxy-3-(6-nitro-3 : 4-dimethoxybenzyl)-coumarone* was obtained in pale yellow needles (1.3 g.), m.p. 100° from methanol, showing a pink reaction with sulphuric acid. (Found : C, 62.7 ; H, 5.0. $C_{18}H_{17}O_6N$ requires C, 63.0 ; H, 5.0 %).

The Lactam (X).—The above nitro-acid (0.15 g.) was dissolved in ammonia (conc., 3 c.c.) and then a solution of ferrous sulphate (1.0 g.) in water was added and the mixture heated on the water-bath for 2 hours. Alkali (2 c.c., 10%) was added and the mixture boiled, filtered and acidified. The crude colorless amino-acid was collected, dried on the porous plate and boiled with acetic anhydride (1 c.c.) for a few minutes. The insoluble *lactam* separated soon, which was collected, washed with dilute alkali and then with alcohol, m.p. > 290°. (Found : N, 3.7. $C_{19}H_{17}O_5N$ requires N, 4.1 %).

Attempted Synthesis of ψ-Trimethylbrazilone.—The foregoing nitro compound (VII : R = NO_2 ; R′ = H) (1.2 g.) in alcohol (8 c.c.) was boiled under reflux with stannous chloride (3 g.) and a few drops of concentrated hydrochloric acid for 2 hours. Alcohol was then removed and the residue boiled with water, tin precipitated with hydrogen sulphide, filtered hot and concentrated. The *hydrochloride* of the *amine* (VII : R = NH_2 ; R′ = H) was obtained as a thick syrup which slowly solidified to long colorless pointed needles, giving a bluish green colour with sulphuric acid. The solution of this hydrochloride in dilute hydrochloric acid (5 c.c.) was diazotised at the room temperature when a large quantity of a yellowish fluffy material, containing nitrogen, separated from which the diazonium salt was filtered (scarlet dye with alkaline β-naphthol) and added to cuprous cyanide solution (KCN 1.1 g., water 7 c.c., copper sulphate 1.0 g.). The yellow product that separated was filtered, dried, extracted with alcohol and concentrated, when the corresponding cyano compound was obtained as a gum, developing with sulphuric acid a pink colour, turning green. The compound did not crystallise. On hydrolysis with alcoholic potash for 24 hours (till the evolution of ammonia was complete), this cyano compound gave a trace of crystalline acidic

material, presumably (VII : R = COOH ; R′ = H), was obtained. The quantity was too meagre to permit isolation and identification.

Acylation of Methyl 6-Methoxy-3-(3 : 4-dimethoxybenzyl) - coumarone-2-carboxylate.—A solution of the ester (0.4 g.) in nitrobenzene (4 c.c.) was cooled to 0° and treated with acetyl chloride (0.2 g.) and stannic chloride (0.8 g.), and the resulting deep blue complex left in the cold for 24 hours. The mixture was decomposed with iced hydrochloric acid, nitrobenzene removed by steam-distillation and the gummy residue hydrolysed with alcoholic sodium hydroxide and the solution acidified. The voluminous jelly-like precipitate became granular on warming. This was collected; it gave a deep red colour with sulphuric acid, turning to bluish red. This acid was heated in a test tube in a metal bath till the evolution of carbon dioxide was over and the material was taken up in benzene and chromatographed on an alumina column. The violet fluorescing column was eluted with benzene and gave on evaporation a crystalline material (0.08 g.), m.p. 241°, identical with 3 : 8 : 9-trimethoxy-6-methyl-β-brazan. (Found : C, 74.2 ; H, 5.8. Calc. for $C_{20}H_{18}O_4$: C, 74.5 ; H, 5.6%).

3 : 8 : 9-*Trimethoxy-6-ethyl-β-brazan* was similarly prepared by employing propionyl chloride. The compound was obtained from pyridine in needles, m.p. and mixed m.p. 154-55°.

Formylation of the ester with *N*-methylformanilide or dimethylformamide did not give encouraging result.

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Chemical Laboraory,
Science College, Patna-5.

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ACIDOID BEHAVIOUR OF CHARCOAL AS A FUNCTION OF ITS OXYGEN COMPLEXES. PART I. ELECTROMETRIC AND CONDUCTOMETRIC TITRATION WITH ALKALIES

By Balwant Rai Puri, Gurcharan Singh and Lekh Raj Sharma

Interaction of sugar charcoal, evacuated at increasing temperatures, with sodium hydroxide and barium hydroxide solutions was studied electrometrically as well as conductometrically, and with calcium carbonate and barium sulphide suspensions only electrometrically. The end-points of the reactions could be easily located from the titration curves. The amounts of the alkalies neutralised were found to agree with those obtained from a volumetric procedure. The values decreased on evacuating charcoal at gradually increasing temperatures. The amounts of calcium carbonate and barium sulphide decomposed by charcoal on heating under reflux were found to correspond to its acidoid value, but in closed bottles at the room temperature, the reactions took place only to the extent of about 50% and 64% respectively. During interaction with alkalies, equivalent amounts of hydroxyl and metallic ions were removed from solution, and the latter were located in the charcoal complex in exchange for its hydrogen ions.

Adsorption of acids and bases by charcoal has been the subject of several investigations (Burnstein *et al.*, *Z. physikal. Chem.*, 1930, **A150**, 421; Bruns *et al.*, *Kolloid Z.*, 1933, **63**, 286; Kolthoff, *J. Amer. Chem. Soc.*, 1932, **54**, 4473; King, *J. Chem. Soc.*, 1937, 1489). Weller and Young (*J. Amer. Chem. Soc.*, 1948, **70**, 4155) have shown that the capacity of charcoal to take up bases increases with the increase in the oxygen content of its surface complex. Puri *et al.* (*Soil Sci.*, 1953, **75**, 209) regard base adsorption by charcoal as a neutralising reaction due to the presence of carbon dioxide in the surface complex. According to them charcoal containing carbon dioxide in the complex, when suspended in water, undergoes surface ionisation as

$$\bigcirc\!\!-CO_2 + H_2O \rightarrow \bigcirc\!\!-CO_3^{2-} \mid 2H^+$$

where the circle represents the charcoal surface. Because of the surface hydrogen ions being directed towards the liquid phase, charcoal behaves as a weak insoluble acid, or "acidoid" to use Michaelis terminology as applied to soils, and reacts with alkalies as

$$\bigcirc\!\!- CO_3^{2-} \mid 2H^+ + Ba(OH)_2 \rightarrow \bigcirc\!\!- CO_3^{2-} \mid Ba^{2+} + 2H_2O.$$

This view has received support from the measurement of heats of neutralisation of different alkalies by charcoal (Puri, Gupta and Lakhanpal, this *Journal*, 1955, **32**, 219).

If the interaction of charcoal with alkalies is a neutralising reaction, as represented above, it should be possible to locate the end-point of the reaction by titrating it electrometrically as well as conductometrically against different alkalies. At the same time equivalent amounts of metal cations should be located in charcoal complex in exchange for H^+ ions.

The literature shows that titration curves of charcoal with alkalies have not been studied in details. Villars (*J. Amer. Chem. Soc.*, 1947, **69**, 214) had been perhaps the only worker to determine p_H vs. ml. of base curves in the case of carbon blacks, but as

there were no points of inflection, he concluded that these substances had no stoichiometric titre in the ordinary sense.

The present paper describes electrometric and conductometric titrations of sugar charcoal, degassed at gradually increasing temperatures, with different alkalies. The amounts of sodium and barium ions exchanged for H^+ ions during the interaction with sodium and barium hydroxides have also been determined.

EXPERIMENTAL

Charcoal.—Sugar charcoal obtained by the carbonisation of pure recrystallised cane sugar and exposed to oxygen at room temperature, as described in the previous work (Puri *et al.*, *loc. cit.*, 1953) was used in these experiments. It was degassed at different temperatures varying from the room temperature to 900°, and the amount of CO_2 given out at each temperature was estimated by passing the gas evolved through a series of flasks containing known amounts of standard solution of barium hydroxide.

Electrometric and Conductometric Titrations.—To 0.5 g. portions of charcoal, contained in 4 oz pyrex bottles, increasing amounts of 0.1 *N*-NaOH or $Ba(OH)_2$ were added and the volume made up to 50 c.c. by the addition of distilled water. The suspensions were shaken for about 48 hours after which the p_H and conductivity values were determined by a Cambridge glass-electrode p_H- meter and a Pye bridge assembly respectively. The potentiometric and conductometric curves obtained with barium hydroxide are plotted in Figs. 1 and 2 respectively.

The electrometric curves with calcium carbonate and barium sulphide were also determined in the case of the sample degassed at room temperature. For this purpose increasing amounts of calcium carbonate and barium sulphide were added to 0.5 g. portions of the charcoal and the volume made up to 50 c.c. by the addition of distilled water. The p_H values were determined after shaking the suspensions for about 48 hours as well as after heating the same under reflux for a further period of 8 hours. The results obtained in cold as well as on heating are plotted in Fig. 3.

Volumetric Titrations.—The amount of alkali [NaOH or $Ba(OH)_2$] neutralised by charcoal was also estimated volumetrically. For this purpose, 1 g. of charcoal was shaken with 80 c.c. of 0.2 *N* alkali for about 48 hours after which the excess of alkali was determined by titrating an aliquot of the clear supernatant liquid against a standard acid solution. This method has been shown (Puri *et al.*, *loc. cit.*, 1953) to give the maximum value for the capacity of charcoal to neutralise alkalies which does not increase further on prolonging the treatment or raising the concentration of the alkali solution.

DISCUSSION

The p_H-titration curves of charcoal with barium hydroxide (Fig. 1) show fairly sharp points of inflection, especially when the temperature of evacuation does not exceed 400°. The buffer capacity of charcoal is seen to decrease gradually with increase in the temperature of its evacuation. A similar curve, obtained in the case of a solution of carbon dioxide, is shown in the same figure. Its resemblance with the titration curves of charcoal is quite evident.

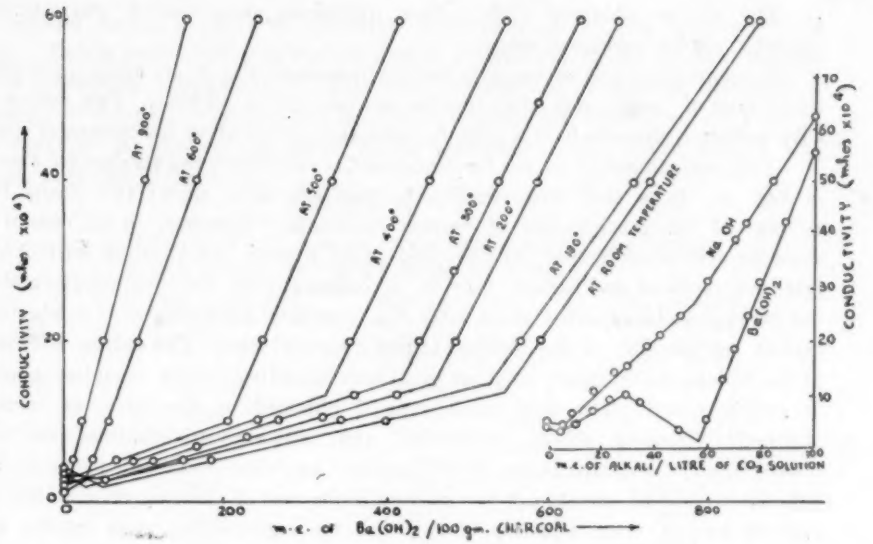

CONDUCTIVITY (mhos x10⁴)
m.e. of Ba(OH)₂ /100 gm. CHARCOAL
AT 900°
AT 600°
AT 500°
AT 400°
AT 300°
AT 200°
AT 100°
AT ROOM TEMPERATURE
NaOH
Ba(OH)₂
m.e. OF ALKALI / LITRE OF CO₂ SOLUTION

FIG. 2

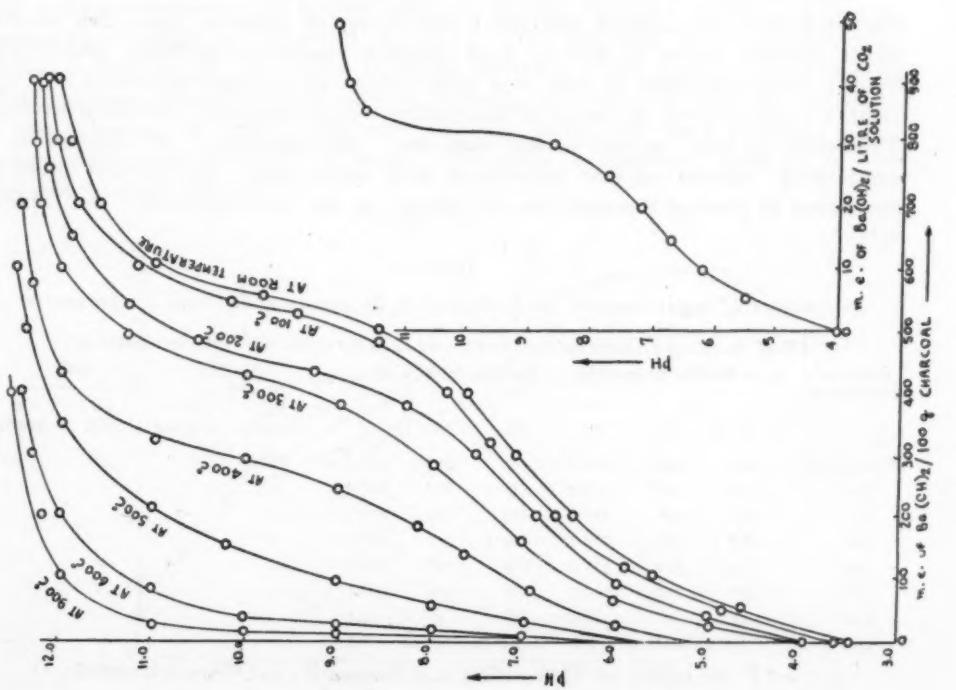

AT ROOM TEMPERATURE
AT 100°
AT 200°
AT 300°
AT 400°
AT 500°
AT 600°
AT 900°
pH
m.e. of Ba(OH)₂/ LITRE OF CO₂ SOLUTION
m.e. of Ba(OH)₂/ 100 g. CHARCOAL

FIG. 1

The curves obtained with sodium hydroxide show similar characteristics and are not given for reasons of space.

The conductometric curves with barium hydroxide (Fig. 2) are again quite characteristic of those of weak acids when titrated against strong alkalies. The curves obtained with sodium hydroxide have similar features and are not given for reasons of space.

The conductometric curves for dissolved CO_2 with both the alkalies are also included in Fig. 2. It is seen that the H_2CO_3—$Ba(OH)_2$ curve shows two sharp breaks on account of the precipitation of barium carbonate. However, in the case of charcoal, since the acid is not in true solution and since during the titration surface hydrogens just get replaced by barium ions in accordance with the equation given above, only one break is to be expected when, after the complete neutralisation, conductivity rises rapidly on account of the addition of free hydroxyl ions. The sodium hydroxide curve of the dissolved CO_2 shows only one break corresponding to the complete neutralisation of carbonic acid. The first break, even if obtained in this case, as mentioned by Kolthoff [*Z. anorg. Chem.*, 1920, **112**, 156; although it is admitted even by him and others (Scott, "Standard Methods of Chemical Analysis", 5th ed., p. 2332) that it is difficult to get it], should not be expected in the case of charcoal since no free carbonate ions are formed (vide equation above) and the conductivity rises rapidly only when excess alkali, after complete neutralisation, is added. The analogy between charcoal and carbon dioxide is therefore limited on account of the nature of the reactions involved.

The amounts of sodium hydroxide and barium hydroxide, neutralised by the charcoal samples evacuated at different temperatures, as indicated from their electrometric titration curves as well as from ordinary volumetric titrations, are shown in Table I. It is interesting to note that these values are in close agreement wich one another irrespective of the nature of the alkali used or the method of estimation involved. This seems to offer support to the view that "base-adsorption" by charcoal is a neutralising reaction as that between an acid and a base. The amount of alkali neutralised by charcoal therefore may be termed as its "base-equivalent" or "acidoid value".

TABLE I

Interaction of sugar charcoal with alkalies on degassing at different temperatures.

Temp. of evacuation.	Alkali (m.e./100 g) required for neutralisation as determined by different methods: Barium hydroxide.			Sodium hydroxide.			$CaCO_3$		BaS	
	E.	C.	V.	E.	C.	V.	In cold.	On heating.	In cold.	On heating.
Room temp.	550	553	556.3	559	553	555.2	259	551	358	557
100°	539	546	553.2	541	547	550.4	...	...	...	...
200°	436	438	441.6	443	439	443.5	...	...	...	...
300°	410	425	422.2	429	431	428.6	...	...	...	...
400°	315	321	325.6	329	326	328 7	...	...	...	...
500°	230	213	223.3	221	220	216.4	...	...	...	...
600°	24	26	28.3	28	33	24.4	...	...	...	...
900°	No indication		Nil	No indication		Nil	...	...	...	...

E, C and V refer respectively to Electrometric, Conductometric and Volumetric methods.

The acidoid value is seen to decrease with increase in the temperature of evacuation. This is probably due to the progressive elimination of the carbon dioxide complex at increasing temperatures. This view is confirmed by the fact that decrease in the capacity of charcoal to neutralise barium hydroxide on evacuating at a particular temperature is almost the same as the amount of CO_2 given out at that temperature, as shown in Table II.

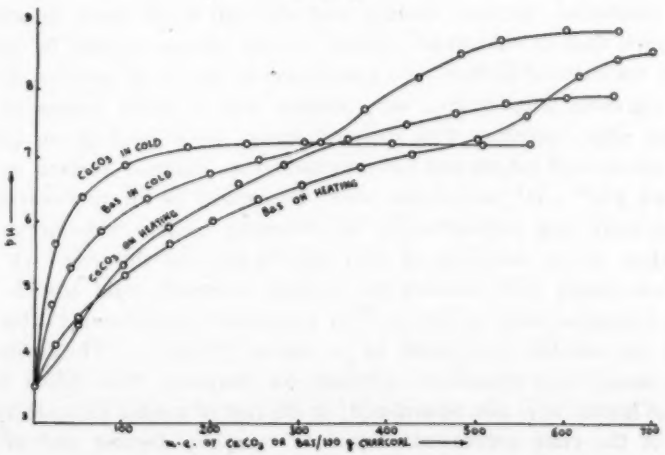
TABLE II

Decrease in the capacity of charcoal to neutralise $Ba(OH)_2$ *in relation to* CO_2 *evolved on evacuating at diff. temp.*

Temp. of evacuation.	$Ba(OH)_2$ neutralised by charcoal (m e./100 g.)	Decrease in the capacity to neutralise $Ba(OH)_2$ (m.e /100 g.)	CO_2 evolved on evacuating at diff. temp. (m.e./100 g.)
Room temp.	556.3	Nil	Nil
100°	553.2	3.1	Nil
200°	441.6	114.7	112.8
300°	422.2	134.1	131.8
400°	325.6	230.7	232.3
500°	223.3	333.0	332.9
600°	28.3	528.0	525.2
900°	Nil	556.3	558.0

Charcoal by virtue of its surface hydrogen ions should be able to bring about decomposition of carbonates and sulphides as well. The titration curves obtained with calcium carbonate and barium sulphide in cold (in closed vessels) as well as on heating under reflux are presented in Fig. 3. The end-point of the reaction with $CaCO_3$ is indicated by the curve becoming horizontal to the x-axis, *i.e.*, any amount added in excess does not alter the p_H value, evidently on account of very low solubility of this substance in water. The curve with BaS, on the other hand, continues to rise because of its greater solubility in water. The point of inflection, however, can be read without much difficulty.

FIG. 3



The amounts of $CaCO_3$ and BaS decomposed by the charcoal (degassed at room temperature) in cold and on heating, as indicated by the titration curves, are included in Table I in appropriate columns. It is seen that on heating under reflux, the amounts decomposed are quite close to the acidoid value of the charcoal, showing that the reactions take place to completion in accordance with the equations,

$$\bigcirc\!\!-CO_3^{2-} \mid 2H^+ + CaCO_3 \rightarrow \bigcirc\!\!-CO_3^{2-} \mid Ca^{2+} + H_2O + CO_2$$

$$\bigcirc\!\!-CO_3^{2-} \mid 2H^+ + BaS \longrightarrow \bigcirc\!\!-CO_3^{2-} \mid Ba^{2+} + H_2S.$$

However, the reactions in closed bottles at the room temperature appear to stop midway on account of the fact that the gases evolved, namely CO_2 and H_2S, do not escape and so set up equilibrium conditions. In this connection it is interesting to note that under such conditions the reaction with $CaCO_3$ takes place to the extent of about 50% and with BaS to the extent of about 64%, in view of the fact that in the former case the same acid, namely carbonic acid, is competing for the base on either side of the equation while in the latter, the acid on the left is twice as strong as that on the right, namely, hydrogen sulphide.

TABLE III

Interaction of alkali-treated charcoal with acid solutions.

Treatment with:	NaOH-treated charcoal. Decrease in the conc. of H^+ ions. (m.e /100 g.)			Sodium salt brought in soln. (m.e./100 g.)	$Ba(OH)_2$-treated charcoal. Decrease in the conc. of H^+ ions. (m.e./100 g.)			Ba salt brought in soln. (m.e./100 g.)
	E.	C.	V.		E.	C.	V.	
HCl	545	553	551.6	549.7	531	533	541.8	536.2
H_2SO_4	548	547	546 8	547.6	...	...	...	...

If the interaction between alkalies and charcoal takes place in accordance with the above views, then an equivalent amount of the cations should be exchanged for H^+ ions on the charcoal surface. In order to verify this, 10 g. portions of the charcoal, degassed at the room temperature, were shaken with a slight excess of NaOH and $Ba(OH)_2$, and after washings with distilled water, were dried in an electric oven at 110°. The amounts of sodium and barium retained on charcoal surface as a result of Na^+—H^+ and $\frac{1}{2}Ba^{2+}$—H^+ exchanges were determined by titrating potentiometrically, conductometrically and volumetrically by following similar techniques, as described before, against $N/10$ solutions of HCl and H_2SO_4 (in the case of Na-charcoal only). It was found that whereas the original charcoal could adsorb no acid, the alkali-treated charcoal could remove acids in equivalent proportions (Table III) to the amounts of the alkalies neutralised by it earlier (Table I). The amounts of sodium and barium brought into solution as chlorides on treatment with dilute HCl (shaking for about 48 hours) were also determined; in the case of sodium chloride by evaporating an aliquot of the clear supernatant liquid to complete dryness and in the case of

barium chloride by precipitating as barium sulphate. The results are included in Table III. On comparing these values with those shown in Table I for the same sample of charcoal (degassed at room temperature), it becomes quite evident that when charcoal is treated with alkalies, both metal cations and hydroxyl anions are removed from solution in equivalent proportions in accordance with the equations given above. Bases are thus "irreversibly adsorbed" by charcoal. On subsequent treatment with acids, hydrogen ions again exchange for metal cations and charcoal regains its original capacity to react with alkalies. This perhaps can be repeated *ad infinitum*.

DEPARTMENT OF CHEMISTRY,
PANJAB UNIVERSITY,
HOSHIARPUR.

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ULTRAVIOLET ABSORPTION SPECTRA OF SULPHONES. PART I. CHELATION IN *o*-HYDROXYSULPHONES

By V. Baliah and (Mrs.) Aleykutty Mathew

The ultraviolet absorption spectra of 2-hydroxydiphenylsulphone, 4-hydroxydiphenylsulphone, 2-hydroxyphenyl-*p* tolylsulphone and 4-hydroxyphenyl-*p*-tolylsulphone in ethanolic and *cyclo*hexane solutions have been determined and compared with those of the corresponding methyl ethers. It is shown that chelation exists in 2-hydroxysulphones.

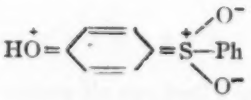
Morton and Stubbs (*J. Chem. Soc.*, 1940, 1347), Burawoy and Chamberlain (*ibid.*, 1952, 2310, 3734) and Burawoy *et al.* (*ibid.*, 1955, 3727) have shown that an internal hydrogen bond displaces the B- and K-bands of phenols to longer wave-lenghts. Thus, these bands in the spectra in hexane of 2-hydroxydiphenyl, 4-hydroxydiphenyl, 3-hydroxybenzaldehyde and 4-hydroxyazobenzene appear at shorter wave-lengths than in the spectra of the corresponding methyl ethers, whereas those of salicylaldehyde, 2-nitrophenol and 2-hydroxy-5-methylazobenzene are observed (in hexane) at longer wave-lengths than the corresponding bands of their methyl ethers. Another important criterion for the presence of an internal hydrogen bond is the characteristic effect of solvents (Burawoy *et al.*, *loc. cit.*). The B- and K-bands of non-chelated phenols are displaced to longer wave-lengths as the dielectric constant of the solvent increases. This is due to the increased polarity of the absorbing system, resulting partly from the dielectric effect of the solvent and partly from the formation of an external hydrogen bond. On the other hand, the bands of chelated phenols are almost unchanged. In these phenols the existence of chelation inhibits the formation of an external hydrogen bond.

Though internal hydrogen-bond formation in compounds containing $-NO_2$, $>CO$ and $-N=N-$ groups has been extensively studied; the same in sulphones has practically remained unexplored till recently. Amstutz *et al.* (*J. Amer. Chem. Soc.*, 1951, **73**, 1220) studied the intramolecular hydrogen bond in certain *o*-substituted sulphones and sulphoxides by an examination of the spectra of these compounds in the infra-red region. They found chelation to occur in *o*-hydroxysulphones and sulphoxides, though the extent of interaction of the *o*-hydroxyl and sulphone groups was much less than that between *o*-hydroxyl and sulphoxide groups, as measured by the displacement of the fundamental absorption band of the OH group. The aim of the present investigation is to study the ultraviolet absorption spectra of some phenolic sulphones and to ascertain whether the electronic spectra data indicate the existence of hydrogen bonding in *o*-hydroxysulphones. The sulphones taken for the investigation were 2-hydroxydiphenyl-, 4-hydroxydiphenyl-, 2-hydroxyphenyl-*p*-tolyl-, 4-hydroxyphenyl-*p*-tolyl-sulphones and their methyl ethers. The spectra were taken both in *cyclo*hexane and in ethanol. The data obtained are summarised in Table I.

TABLE I

Sulphone.	In *cyclo*hexane. Phenol. $\lambda_{max.}$	ϵ.	Methyl ether. $\lambda_{max.}$	ϵ.	In 25% ethanol. Phenol. $\lambda_{max.}$	ϵ.	Methyl ether. λ_{max}	ϵ.
2-Hydroxydiphenyl-	295 mμ	4600	295 mμ	6600	295 mμ	4200	290 mμ	4600
	275	2500	285	6100	233	12600	235	12000
	238	10700	232	14600	220	16400	219	16400
			219	17100				
4-Hydroxydiphenyl-					295	4600		
	247	13000	252	18900	255	14100	254	18800
2-Hydroxyphenyl-	294	4900	285	4100	294	4400	290	4700
p-tolyl	244	14600	238	16000	238	15200	240	16100
			223	15000	225	14800	224	15500
4-Hydroxyphenyl-	249	16500	253	20700	294	4200		
p-tolyl-	225	9400	227	11000	256	16000	255	21000
			221	10700	223	12400	228	12000

Analysis of Spectra obtained in cyclo*Hexane.*—Considering the absorption spectra of the hydroxy compounds alone, the following observations may be made: The B-bands are seen in *o*-hydroxysulphones, while they are not seen in *p* hydroxysulphones. Presumably these bands are masked in *p*-hydroxysulphones. The appearance of the B-bands in *o*-hydroxysulphones can be explained on the basis of the formation of an internal hydrogen bond. Such a bond increases the polarity of the absorbing system in the ground state and this in turn can increase the intensity of the B-band, making it visible. Such a postulate may be expected to have other consequences, e.g. the increased polarity should displace the K-band also to a longer wave-length. This is seen not to be the case. In fact, the *p*-hydroxysulphone absorbs (K-band) at a longer wave-length. The explanation for this might be that the *p*-isomer has a longer conjugated system in the excited state.



It would be of interest to make such a comparison in the case of isomeric *o*- and *p*-hydroxy aldehydes, ketones, nitrobenzenes etc. But unfortunately comparable data, though available in alcohol solution, are not available in a non-polar solvent like hexane or *cyclo*hexane (cf. Morton and Stubbs, *loc. cit.*, Burawoy and Chamberlain, *loc. cit.*, Burawoy *et al.*, *loc. cit.*). In these papers are recorded the ultraviolet absorption data in hexane solution for *o*-hydroxy compounds but not for *p*-hydroxy compounds, presumably due to the latter having a very low solubility in hexane. Even in the present investigation the *p*-hydroxysulphones were found to be only feebly soluble in *cyclo*hexane. Solutions of the required concentration could, however, be obtained by dissolving a small amount of the substance in a large volume of the solvent.

Effect of Methylation on B- and K-bands in cyclo*Hexane.*—Methylation of a hydroxyl group *para* to the sulphonyl group has caused a slight shift of the B- and K-bands to longer wave-lengths with increase in intensity. This is the normal effect of methylation, in agreement with the greater electron-releasing power of the methyl group. On the other hand, methylation of a hydroxyl group in the *ortho* position resulted in a hypsochromic displacement of both the bands. These facts clearly establish the existence of chelation in *o*-hydroxysulphones,

Analysis of Spectra obtained in Ethanol.—Methylation displaces the B-bands of *o*-hydroxysulphones to shorter wave-lengths, the intensity being almost unaffected. The B-bands are not observed for the methyl ethers of *p*-hydroxysulphones, since they are masked by the more intense K-bands.

The effect of methylation on K-bands in ethanol is interesting. While in the case of *p*-hydroxysulphones methylation caused a hypsochromic shift, a bathochromic shift occured for *o*-hydroxysulphones. This is just the reverse of what happens in *cyclo*hexane. The observed shifts to shorter wave-lengths are due to a reversal of the bathochromic effect of hydrogen-bond formation with the solvent.

Effect of Solvent and Detection of Chelation.—The B- and K-bands of phenols in which no chelation occurs are known to shift to longer wave-lengths with increase in the dielectric constant of the solvent (Burawoy *et al.*, *J. Chem. Soc.*, 1955, 3723). The present investigation has also revealed that a change from *cyclo*hexane to ethanol displaces the K-band of *p*-hydroxysulphones to longer wave-lengths (B-band not observed in *cyclo*hexane). On the other hand, the B-bands of the *o*-hydroxysulphones are almost unaffected on changing the solvent from *cyclo*hexane to ethanol. The K-bands are, however, displaced to shorter wave-lengths. This is significant in view of the fact that the K-bands of salicylaldehyde, 2-hydroxy-5-methylazobenzene and 2-nitrophenol are almost unchanged by changing the solvent from hexane to ethanol (Burawoy *et al.*, *J. Chem. Soc.*, 1955, 3728). The explanation for this seems to be that the $-SO_2-$ group forms weaker chelate links than the -CHO, -N=N-, or $-NO_2$ group and that the chelation in *o*-hydroxysulphones becomes weak in polar solvents like ethanol.

EXPERIMENTAL

Spectra were determined using a Beckman ultraviolet spectrophotometer, model DU. The *o*- and *p*-hydroxysulphones, and their methyl ethers were prepared as described in an earlier paper (this *Journal*, 1954, **31**, 513). The ethanol (95%) used as solvent was purified by distillation after treatment with lead acetate and sodium hydroxide. The *cyclo*hexane used was purified by passing through a column of silica gel several times ; it boiled at 81°.

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DEPARTMENT OF CHEMISTRY,
ANNAMALAI UNIVERSITY,
ANNAMALAINAGAR.

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SYNTHESIS OF DIHALOGENATED 5-AMINOACRIDINE DERIVATIVES

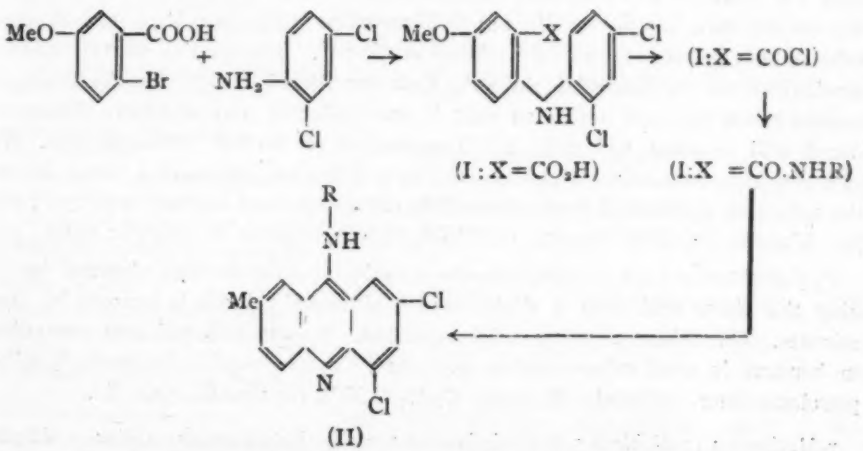
By A. G. Munshi*, K. S. Nargund and P. M. Dholkia†

Several dihalogenated-5-substituted aminoacridines and their methoxy derivatives have been described.

A large amount of work has been done to prepare suitable acridine and quinoline derivatives as antimalarial drugs (cf. Wiselogle, "Survey of Antimalarial Drugs", 1941-45, Vol. II, Part II). Magidson and Grigorovsky (*Ber.*, 1936, **69**, 396) observed that 5-aminoacridine derivatives containing chlorine in any position exhibited antimalarial property. Whitmore *et al.* (*J. Amer. Chem. Soc.*, 1946, **68**, 1596) synthesised 2 : 8-dichloro-5(δ-diethylamino-α-methylbutyl)-aminoacridine and reported it to have a better antimalarial property than atabrine.

With a view to ascertaining whether the dichloroacridine derivatives in general possess the antimalarial property or the particular positions occupied by two chlorine atoms confer this property, and also keeping in view the fact that the presence of the methoxy group greatly increases the lipoid solubility of the drug (Shaw, *Amer. J. Hyg.*, 1928, **8**, 505), synthesis of several dichloro-5-(δ-diethylamino-α-methylbutyl)-aminoacridines and their 7-methoxy derivatives has been undertaken.

The general method of preparation of the above dihalogenated 5-aminoacridine derivatives consists in condensation of the requisite dichloroaniline with *o*-chloro- or *o*-bromo-benzoic acid derivatives, cyclisation of the resulting products and finally attachment of various dialkylaminoalkyl-amines. The reactions may be represented as shown below :



(II)

[R= (*i*) CH_3-CH-$(CH_2)_3$-NEt_2 (*iii*) -$(CH_2)_3$-$N(CH_3)_4$
(*ii*) —$(CH_2)_3$—$N(CH_3)_4O$ (*iv*) -$(CH_2)_3$—NEt_2]

* Present address : Lalan College, Bhuj.
† In part.

Condensation of 2:4-dichloroaniline with 6-bromo-3-methoxybenzoic acid was carried cut under the conditions of Ullmann *et al.* (*Ber.*, 1905, **38**, 2125; *Annalen*, 1907, **355**, 322; Meister, Lucein and Brunning, Ger. Pat. 145789), 2′:4′-dichloro-4-methoxydiphenylamine-2-carboxylic acid (I: X = CO_2H) being obtained. It was found that nitrobenzene was a more suitable solvent than *iso*amyl alcohol, as the reaction could be carried out at a higher temperature with better yields. (I: X=CO_2H) was then treated with thionyl chloride in benzene solution to obtain its acid chloride (I: X=COCl), the benzene solution of which was treated with the necessary amine to obtain the corresponding amide (I: X=CO.NHR), which was then cyclised by treating the same solution with phosphorus oxychloride without isolating (I: X=CO.NHR), when the acridine (II) was obtained as a dihydrochloride in the manner indicated in the Experimental. In some cases the dihydrochloride had very low melting point. Repeated crystallisation or precipitation did not improve the nature of the product. In such cases the product was dried at about 100° for one hour. The m.p. and analysis of such a sample are reported. In certain cases, only in working up at the final stage, the reaction mixture was extracted with alcohol and the hydrochloride of the condensed product was precipitated by the addition of either ether or acetone; while in some cases, the reaction mixture was poured into ice and liquor ammonia, and the base, thus precipitated, was collected, washed with ether and dried. It was generally purified by crystallisation from absolute alcohol. The hydrochloride was then prepared by dissolving the base in absolute alcohol or ether and passing a current of dry hydrochloric acid gas into the solution.

EXPERIMENTAL

2′:4′-Dichloro-4-methoxydiphenylamine-2-carboxylic acid was prepared by refluxing the mixture of 6-bromo-3-methoxybenzoic acid (7.0 g., 0.1*M*), anhydrous potassium carbonate (4.5 g., 0.11*M*), 2:4 dichloroaniline (5.1 g., 0.11*M*), a trace of copper powder and nitrobenzene (30 c.c.) for 5 hours at 160-70°. The reaction mixture was then steam-distilled and the residual liquid in the flask was filtered. On cooling the filtrate, the potassium salt of the acid separated out; it was collected and acidified. The green-coloured acid obtained had m.p. 230°, unchanged on further crystallisations. The filtrate after separation of the potassium salt, on acidification, also gave a small amount of the same acid, crystallised from acetic acid in pale green small needles, m.p. 230°, yield 55%. (Found: Cl, 22.94; equiv., 312. $C_{14}H_{11}O_3NCl_2$ requires Cl, 22.76%; equiv., 312).

2′:4′-Dichloro-4-methoxydiphenylamine-2-carboxyl chloride was obtained by refluxing the above acid with a slight excess of thionyl chloride in benzene for about 20 minutes. On cooling a yellow solid separated. It was collected and crystallised from benzene in small yellow needles, m.p. 142°. It was found to be sparingly soluble in petroleum ether. (Found: Cl, 32.59. $C_{14}H_{10}O_2NCl_3$ requires Cl, 32.23%).

7-Methoxy-1:3-dichloro-5-(δ-diethylamino-α-methylbutyl)-aminoacridine dihydrochloride was obtained by heating the mixture of the above acid chloride (1 g.), dry benzene (30 c.c.) and δ-diethylaminomethylbutylamine (0.47 g.) for half an hour. Benzene was removed by distillation; $POCl_3$ (3 c.c.) was then added to the reaction mixture, and refluxed for 3 hours. On removing $POCl_3$ by washing with petroleum ether

TABLE I

	Products.	M.P.	Cryst. from..	Formula.	% Chlorine. Found.	% Chlorine. Calc.
(1)	3′:5′-Dichloro-4-methoxydiphenylamine-2-carboxylic acid	221°	Acetic acid	$C_{14}H_{11}O_3NCl_2$	22.4	22.8
(2)	Acid chloride of (1)	125°	Petrol ether	$C_{14}H_{10}O_2NCl_3$	32.8	32.2
(3)	7-Methoxy-2:4-dichloro-5-(δ-diethylamino-α-methylbutyl)-aminoacridine dihydrochloride	235°	Alcohol-acetone	$C_{23}H_{30}ON_3Cl_4$	28.4 (8.0)	28.0 (8.2)
(4)	7-Methoxy-2:4-dichloro-5-(γ-morpholinopropyl)-aminoacridine dihydrochloride	249°	Absolute alcohol	$C_{20}H_{25}O_2N_3Cl_4$	29.0	28.8
(5)	7-Methoxy-2:4-dichloro-5-(γ-piperidinopropyl)-aminoacridine dihydrochloride	225° (decomp.)	Alcohol-ether	$C_{22}H_{27}ON_3Cl_4$	29.3	29.9
(6)	7-Methoxy-2:4-dichloro-5-(γ-diethylaminopropyl)-aminoacridine dihydrochloride	237° (decomp.)	Alcohol-acetone	$C_{21}H_{27}ON_3Cl_4$	29.9	29.65
(7)	2:4-Dichloro-5-(γ-morpholinopropyl)-aminoacridine dihydrochloride	271°	Absolute alcohol	$C_{20}H_{23}ON_3Cl_4$	31.0	30.7
(8)	2:4-Dichloro-5-(δ-diethylamino-α-methylbutyl)-aminoacridine dihydrochloride	170°	Alcohol-acetone	$C_{23}H_{29}N_3Cl_4$	30.1 (8.71)	30.9 (8.8)
(9)	2:4-Dichloro-5-(γ-diethylaminopropyl)-aminoacridine dihydrochloride	255°	Absolute alcohol	$C_{20}H_{25}N_3Cl_4$	31.9	31.6
(10)	2′:4′-Dichloro-4-methoxydiphenylamino-2-carboxylic acid	230°	Acetic acid	$C_{14}H_{11}O_3NCl_2$	22.9	22.8
(11)	Acid chloride of (10)	142°	Benzene	$C_{14}H_{10}O_2NCl_3$	32.6	32.2
(12)	7-Methoxy-1:3-dichloro-5-(δ-diethylamino-α-methylbutyl)-aminoacridine dihydrochloride	191°	Alcohol-ether	$C_{23}H_{31}ON_3Cl_4$	28.2 (8.04)	28.0 (8.2)
(13)	7-Methoxy-1:3-dichloro-5-(γ-morpholinopropyl)-aminoacridine dihydrochloride	285°	Alcohol	$C_{20}H_{27}ON_3Cl_4$	29.1	28.9
(14)	1:3-Dichloro-5-(γ-piperidinopropyl)-aminoacridine dihydrochloride	220°	Abs. alcohol-ether	$C_{21}H_{25}N_3Cl_4$	31.0	30.9
(15)	1:3-Dichloro-5-(δ-diethylamino-α-methylbutyl)-aminoacridine dihydrochloride	300°	Alcohol-acetone	$C_{23}H_{29}N_3Cl_4$	29.9 (8.69)	29.9 (8.8)
(16)	2′:5′-Dichloro-4-methoxydiphenylamine-2-carboxylic acid	216°	Acetic acid	$C_{14}H_{11}O_3NCl_2$	22.83	22.76
(17)	Acid chloride of (16)	104°	Benzene	$C_{14}H_{10}O_2NCl_3$	32.41	32.23
(18)	7-Methoxy-1:4-dichloro-5-(γ-morpholinopropyl)-aminoacridine dihydrochloride	236°	Alcohol	$C_{21}H_{25}O_2N_3Cl_4$	29.01	28.8
(19)	7-Methoxy-1:4-dichloro-5-(γ-piperidinopropyl)-aminoacridine dihydrochloride	150° (decomp.)	,,	$C_{22}H_{27}ON_3Cl_4$	29.11	28.92
(20)	7-Methoxy-1:4-dichloro-5-(δ-diethylamino-α-methylbutyl)-aminoacridine dihydrochloride	185°	Alcohol	$C_{23}H_{31}ON_3Cl_4$	28.26	28.0
(21)	1:4-Dichloro-5-(γ-morpholinopropyl)-aminoacridine dihydrochloride	175°	,,	$C_{20}H_{27}ON_3Cl_4$	30.96	30.7
(22)	1:4-Dichloro-5-(γ-piperidinopropyl)-aminoacridine dihydrochloride	250°	,,	$C_{21}H_{25}N_3Cl_4$	30.99	30.9
(23)	1:4-Dichloro-5-(δ-diethylamino-α-methylbutyl)-aminoacridine dihydrochloride	325°	,,	$C_{22}H_{29}N_3Cl_4$	29.90	29.9

the residue was extracted with absolute alcohol and the yellow dihydrochloride was precipitated by adding excess of dry ether. It was then purified by redissolving in fresh alcohol and reprecipitating as above dried product, m.p. 192-93° (decomp.). (Found : Cl, 28.21. $C_{23}H_{31}ON_3Cl_4$ requires Cl, 28.0%).

7-Methoxy-1 : 3-dichloro-5-(γ-morpholinopropyl)-aminoacridine dihydrochloride was similarly prepared by condensing the above acid chloride with γ-morpholinopropylamine. It crystallised from alcohol in yellow granular solid, m.p. 285° (decomp.). (Found : Cl, 29.01. $C_{21}H_{25}O_2N_3Cl_4$ requires Cl, 28.8%).

For the sake of brevity, various substituted diphenylamine-2-carboxylic acids with their acid chlorides and various substituted 5-aminoacridine dihydrochlorides are recorded in Table I.

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M. R. Science Institute,
Gujarat College,
Ahmedabad 6.

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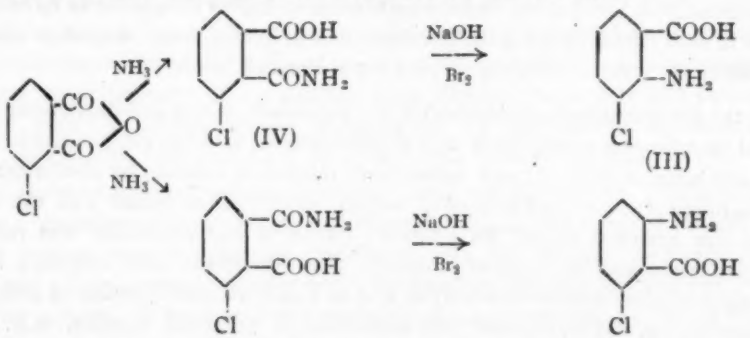
SYNTHESIS IN ACRIDINE SERIES. PART III. SYNTHESIS OF 5-N-SUBSTITUTED 1:9- AND 2:9-DICHLOROACRIDINES

G. S. Patel, S. R. Patel and K. S. Nargund

5-(δ-Diethyl-amino-α-methylbutyl)-amino-2:9- and -1:9-dichloroacridines have been synthesised by cyclisation of the amides obtained from the required amine and the acid chloride of 5:2′-dichloro-(I) and 6:2′-dichloro- (II) diphenylamine-2-carboxylic acid respectively.

In a previous communication (Patel and Nargund, this *Journal*, 1955, **32**, 770) synthesis of 3:7- and 3:9-dichloro-5-N-substituted acridine derivatives has been described. In continuation of this series, the present paper deals with the synthesis of the corresponding 1:9- and 2:9-dichloroacridine derivatives.

The Ullmann condensation of 4:2-dichlorobenzoic acid with *o*-chloroaniline failed to afford the expected 5:2′-dichlorodiphenylamine-2-carboxylic acid (I), when the condensation was attempted in presence of various solvents like amyl alcohol, xylene and nitrobenzene at temperatures varying from 120° to 200°. Ultimately, when the reaction was carried out in absence of a solvent using *o*-chloroaniline in excess, (I) was obtained in about 50% yield. In this connection it would be interesting to note that Whitmore *et al.* (*J. Amer. Chem. Soc.*, 1946, **68**, 1596) reported that 2′:4-dichlorobenzoic acid, on similar condensation with *m*-chloroaniline, using methyl*cyclo*hexanol as solvent, furnished 5:3′-dichlorodiphenylamine-2-carboxylic acid in only about 6% yield.



6:2′-Dichlorodiphenylamine-2-carboxylic acid (II) was obtained on condensation of 3-chloroanthranilic acid with *o*-chloro-iodobenzene, using the latter in excess in place of a solvent. Chaudhry and Nargund (*J. Univ. Bombay*, 1951, **19**, 65, 68) have synthesised 3-chloroanthranilic acid (III) by two different methods, viz., (*i*) by oxidation

of 7-chloroisatin and (*ii*) by Hoffmann's degradation of 3-chlorophthalimide. The method described here is a modification of the latter method and in this the phthalamic acid, obtained on treatment of 3-chlorophthalic anhydride with ice-cold liquor aminonia, was subjected to Hoffmann's degradation to furnish (III) as the only product of the reaction. This indicated that the anhydride ring opened up only in one way, affording 2-amido-3-chlorobenzoic acid (IV); on opening in the other manner, 2-amido-6-chlorobenzoic acid (V) would have been obtained and which on Hoffman's degradation would have furnished 6-chloroanthranilic acid (VI).

5 : 2′-Dichloro- and 6 : 2′-dichloro-diphenylamine-2-carboxylic acids on reaction with phosphorus oxychloride afforded the corresponding dichloroacridones, instead of the expected corresponding 5-chloroacridine derivatives. Hence, the facile method (Magidson and Grigorovsky, *Ber.*, 1936, **69**, 396) of obtaining 5-N-substituted aminoacridine derivatives by condensing the corresponding 5-chloroacridine derivative with the required amine was not applicable. 1 : 9-Dichloro- and 2 : 9-dichloro-5-N-substituted acridine derivatives, described in this communication, were therefore obtained from the acid chlorides of (II) and (I) respectively, and the required amines were isolated as hydrochlorides. In some cases the hydrochlorides were obtained as slightly sticky solids, due to the traces of moisture associated with them and had to be treated by heating them under reduced pressure in order to obtain the product suitable for characterisation.

EXPERIMENTAL

5:2′-Dichlorodiphenylamine-2-carboxylic Acid.—When the condensation of 2:4-dichlorobenzoic acid (1*M*) with *o*-chloroaniline (1*M*) was carried out in presence of potassium carbonate (1 *M*) and a trace of Cu powder and solvents like amyl alcohol and xylene at temperatures from 120° to 150°, and nitrobenzene at higher temperatures up to 200°, the reaction in each case failed, 2 : 4-dichlorobenzoic acid having been recovered unchanged. The condensation was successfully carried out as detailed below.

To the dry voluminous precipitate of the potassium salt of 2 : 4-dichlorobenzoic acid, obtained by refluxing a mixture of 2 : 4-dichlorobenzoic acid (10 g.), potassium carbonate (10 g.) and benzene (10 c. c.) and subsequent removal of benzene by distillation at 100°, *o*-chloroaniline (30 c.c.) and a trace of copper powder were added and the resulting mixture was heated at 165-70° for 3 hours. Excess of *o*-chloroaniline was removed by steam-distillation and the residual solution, after treatment with charcoal, furnished 5 : 2′-dichlorodiphenylamine-2-carboxylic acid as a light coloured powder on acidification; yield (crude), 7 g. It crystallised from acetic acid in yellowish needles, m.p. 228-29°. (Found : Equiv., 284; N, 4.85; Cl, 25.5. $C_{13}H_9O_2NCl_2$ requires equiv., 282; N, 4.9; Cl, 25.2%).

5:2′-Dichlorodiphenylamine-2-carboxylic acid chloride was obtained by heating the above acid (1 part) and thionyl chloride (5 parts) for half an hour and on subsequent distillation of the excess of thionyl chloride under reduced pressure. The crude acid chloride was sufficiently pure for its use in the subsequent operation. It crystallised from petroleum ether, m.p. 100-101°. (Found : Cl, 35.7. $C_{13}H_8ONCl_3$ requires Cl, 35.4%).

2 : 9-*Dichloro*-5 - (δ-*diethylamino* - α-*methylbutyl*)-*aminoacridine hydrochloride* was prepared by cyclisation of the acid amide obtained on reacting the above mentioned acid chloride with δ-diethylamino-α-methylbutylamine, following the method described in the previous communication (*loc. cit.*). The hydrochloride was dissolved in a minimum quantity of absolute alcohol and the solution was diluted with three times the quantity of acetone and kept overnight, when the hydrochloride separated as a yellow solid. Due to traces of moisture in it, it could not be powdered well for the determination of its m.p. and so it was dried by heating it at 80°/50 mm for half an hour ; m.p. of the dried sample, 165-70° (decomp.). The sample was used for analysis. (Found : N, 7.9 ; Cl, 28.1. $C_{22}H_{29}N_3Cl_4$, $2H_2O$ requires N, 8.1 ; Cl, 27.8 %).

2 : 9-*Dichloro*-5 (γ-*morpholinopropyl*)-*aminoacridine dihydrochloride* was obtained similarly from 5 : 2′-dichlorodiphenylamine-2-carboxylic chloride and γ-morpholinopropylamine. It crystallised from alcohol-acetone mixture in yellow granules, m.p. 245-47° (decomp.). (Found : N, 8.9 ; Cl, 31.5. $C_{20}H_{23}ON_3Cl_4$ requires N, 9.0 ; Cl, 30.8%).

3-*Chlorophthalamic Acid* (2-*Amido*-3-*chlorobenzoic Acid*).—3-Chlorophthalic anhydride (1 g.), obtained by treating 3-chlorophthalic acid with acetic anhydride (Chaudhry and Nargund, *loc. cit.*), was stirred in ice-cold liquor ammonia (3 c.c.) till it dissolved. This solution was acidified with HCl and after some time the acid slowly crystallised out from the acidified solution in small white plates, m.p. 235-37°. (Found : Equiv., 194 ; Cl, 17.6. $C_8H_6O_3NCl$ requires equiv., 199 ; Cl, 17.7%).

Hoffmann's Degradation of 3-*Chlorophthalamic Acid*: *Formation of* 3-*Chloroanthranilic Acid*.—3-Chlorophthalamic acid (2.5 g.) was dissolved in ice-cold *N*-KOH solution (25 c.c.) and then mixed with a solution of bromine (1 c.c.) in 25 c.c. of the same alkali solution, kept cool in an ice-bath. To this further quantity KOH solution (25 c.c.) was added and the resulting mixture was stirred for some time. The reaction flask was then removed and the temperature was slowly raised to 80°, after which heating was continued for half an hour. The reaction mixture was then cooled and just neutralised with calculated quantity of 2*N*-HCl and cooled in an ice-bath when 3-chloroanthranilic acid slowly separated out. It crystallised from dilute acetic acid in pale yellow plates, m.p. 183°, yield 1 g. (Chaudhry and Nargund, *loc. cit.*, record the same melting point). (Found : Equiv., 168 ; Cl, 20.4. Calc. for $C_7H_6O_2NCl$: Equiv., 171 ; Cl, 20.7%).

6 : 2′-*Dichlorodiphenylamine*-2-*carboxylic Acid*.—A mixture of 3-chloroanthranilic acid (5 g.), potassium carbonate (4 g.) and benzene (10 c.c.) was refluxed for half an hour and the benzene was removed by distillation. To the residue *o*-chloroiodobenzene (30 c.c.) and a trace of copper powder were added and the reaction mixture was refluxed at 165-70° for 3 hours. Excess of *o*-chloroiodobenzene was removed by steam-distillation and the dark coloured solution after treatment with charcoal was filtered and acidified to obtain 6 : 2′-dichlorodiphenylamine-2-carboxylic acid as a pale yellow solid. It crystallised from acetic acid in pale yellow small needles, m.p 176-78°, yield 6 g. (Found : Equiv., 280 ; N, 4.8. $C_{13}H_9O_2NCl_2$ requires equiv., 282 ; Cl, 25.2%).

6 : 2′-*Dichlorodiphenylamine*-2-*carboxylic chloride* was obtained from the above acid on treatment with thionyl chloride. It crystallised from petroleum ether in yellow plates, m.p. 89-90°. (Found : Cl, 35.7. $C_{13}H_8ONCl_3$ requires Cl, 35.4%).

1 : 9-*Dichloro*-5-(δ-*diethylamino*-α-*methylbutyl*)-*aminoacridine hydrochloride* was obtained, as indicated above, starting with 6 : 2′-dichlorodiphenylamine-2-carboxylic chloride. The hydrochloride, which separated out as a yellow solid from a mixture of alcohol-acetone, could not be powdered well. It was therefore dried at 80°/50 mm. This sample melted at 155 60° (decomp.) and the same used for analysis. (Found : N, 7.85 ; Cl, 28.0. $C_{22}H_{29}N_3Cl_4$, $2H_2O$ requires N, 8.1 ; Cl, 27.8%).

1 : 9-*Dichloro*-5-(γ-*morpholinopropyl*)-*aminoacridine dihydrochloride* was obtained by similarly using γ-morpholinopropylamine. It crystallised from alcohol in yellow crystalline powder, m.p. 232-34°. (Found : N, 8.8 ; Cl, 31.3. $C_{20}H_{23}ON_3Cl_4$ requires N, 9.0 ; Cl, 30.8%).

M. R. Science Institute,
Gujarat College, Ahmedabad.

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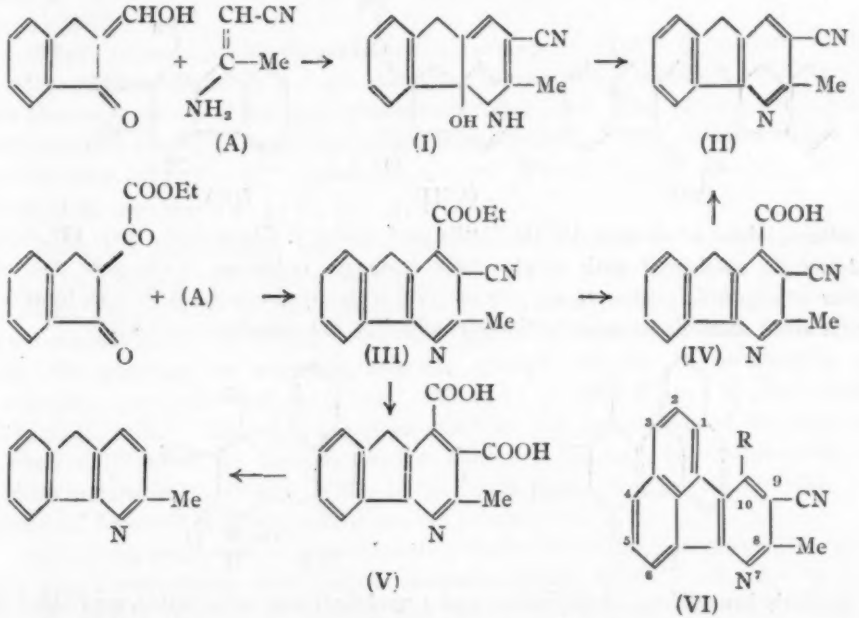
SYNTHESIS IN THE 4-AZAFLUORENE GROUP. PART II. SYNTHESIS OF 4-AZAFLUORENES AND 7-AZAFLUORANTHENES

By J. N. Chatterjea and K. Prasad

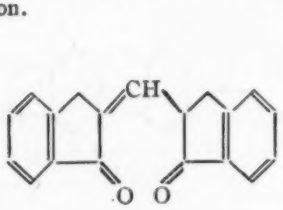
Synthesis of some 4-azafluorenes from 1-indanone is described. Extension of the methods used to the synthesis of 7-azafluoranthenes from acenaphthenone.

A general method of synthesis of the 4-azafluorene ring system from 2-phenylpyridine-3-carboxylic acids has been described in an earlier communication (this *Journal*, 1955, **32**, 371). It appeared desirable, however, to effect a more direct synthesis from indane derivatives. This has been achieved according to the scheme presented below.

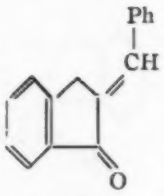


2-Hydroxymethylene-1-indanone on treatment with 2-aminocrotononitrile in absolute alcohol afforded the hydroxy compound (I) which on heating was converted into 2-cyano-3-methyl-4-azafluorene (II). This was obtained in a better yield from the related carboxylic acid (IV), obtainable from 1-indanone-2-glyoxylic ester, as shown above. Hydrolysis of the cyano-ester (III) gave 3-methyl-4-azafluorene-1 : 2-dicarboxylic acid (V), which on decarboxylation afforded 3-methyl-4-azafluorene, identified through the picrate. In an analogous manner, acenaphthenone was converted into the corresponding glyoxylic ester which gave the 7-azafluoranthene (VI : R = CO_2Et) on condensation with 2-aminocrotononitrile.

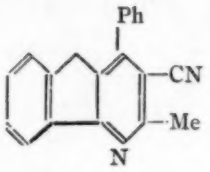
When 2-aminocrotononitrile was replaced by ethyl 2-aminocrotonate, the outcome was unexpected. With an excess of the ester and 2-hydroxymethylene-1-indanone at the room temperature, the sole product was a light yellow crystalline material (m.p. 166°) for which accurate analytical data were difficult to obtain. The compound analysed for $C_{20}H_{22}O_2N_2$ and gave the hydroxymethylene compound and ammonia on treatment with warm alkali. On heating above the melting point or on treatment with mineral acids, a new compound ($C_{19}H_{19}O_3N$, m.p. 268°) was formed which on boiling with alcoholic sodium hydroxide afforded a steel-blue sodium salt, identified as the sodium salt of the diketone (VII), $C_{19}H_{14}O_2$ of Ruhemann and Levy (*J. Chem. Soc.*, 1912, **101**, 2549). It therefore appears that the products mentioned above are "ammonia derivatives" of 2-hydroxymethylene-1-indanone or the condensation products thereof. Yet another unidentified product, m.p. 214°, was obtained by the condensation of 2-hydroxymethylene-1-indanone with ethyl 2-aminocrotonate in dry ethanolic solution.



(VII)

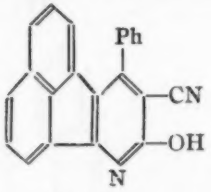


(VIII)

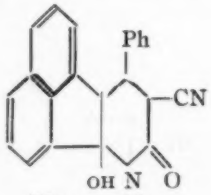


(IX)

2-Benzylidene-1-indanone (VIII) (Mills and Akers, *J. Chem. Soc.*, 1925, **127**, 2475) could not be condensed with ethyl 2-aminocrotonate in boiling acetic acid solution (Petrow *et al.*, *ibid.*, 1949, 2134); the reaction with 2-aminocrotonitrile was, however, brought about in alcoholic sodium ethoxide, affording the 4-azafluorene (IX).



(X)



(XI)

Similarly benzylidene-, *p*-tolylidene- and 1-naphthylidene-acenaphthenone yielded the 7-azafluoranthenes [VI: R = Ph; R = $C_6H_4CH_3$ (*p*) and R = $C_{10}H_7$ (α)]. Benzylidene-acenaphthenone was also condensed with cyanoacetamide to yield 7-azafluoranthenes. The product depended on the condensing agent. For example, with alcoholic sodium ethoxide (X) was the sole product, whereas with diethylamine as a catalyst, the product was (XI).

EXPERIMENTAL*

2-Cyano-3-methyl-4-α-hydroxy-4:4-α-dihydro-4-azafluorene (I).—Equimolecular quantities of 2-hydroxymethylene-1-indanone and 2-aminocrotonitrile in 10 times their

* All m.p. s are uncorrected.

weight of dry alcohol were allowed to remain at the room temperature for 3 days. The yellowish mass separating was collected. The *hydroxy-azafluorene* (I) was obtained as yellow needles, m.p. 232° from alcohol, yield *ca.* 30%. (Found: C, 74.5; H, 5.8; N, 12.5. $C_{14}H_{12}ON_2$ requires C, 75.0; H, 5.4; N, 12.5%). With commercial absolute alcohol, the yield was poorer and the compound impure. The condensation may also be brought about in poor yield in dry ethereal solution.

6:7-*Dimethoxy derivative* of (I) was prepared in a similar way from 2-hydroxymethylene-5:6-dimethoxy-1-indanone and obtained in yellow crystalline mass, m.p. 300-302° from alcohol. (Found: C, 67.0; H, 6.0. $C_{16}H_{16}O_3N_2$ requires C, 67.6; H, 5.6%).

2-*Cyano*-3-*methyl*-4-*azafluorene* (II).—The foregoing compound (I) was heated for 15 minutes at 280° (metal bath) in vacuum and the product collected on a cold finger. The compound (II) was obtained as colorless needles from alcohol, m.p. 183-84°, yield 40-50%. (Found: C, 82.0; H, 4.8; N, 14.4. $C_{14}H_{10}N_2$ requires C, 81.5; H, 4.9; N, 13.6%).

Ethyl 2-*Cyano*-3-*methyl*-4-*azafluorene*-1-*carboxylate* (III).—A mixture of ethyl 1-indanone-2-glyoxylate (3 g.) and 2-aminocrotononitrile (1 g.) in dry alcohol (10 c.c.) was allowed to remain at the room temperature for 14 days. The product (III) (0.95 g.) that separated was collected and crystallised from alcohol. It was obtained in long silky needles, m p. 174-75°. λ_{alc}^{max} 2750 Å (log ϵ, 3.01). (Found: C, 73.9; H, 5.2; N, 10.4. $C_{17}H_{14}O_2N_2$ requires C, 73.4; H, 5.0; N, 10.1%).

When the condensation was attempted in dry benzene at the room temperature for 4 days, a crop of light yellow needles, m.p. 128-32°, was obtained. All attempts to purify the material by crystallisation resulted in decomposition with the regeneration of the original ester. On boiling with dilute alkali, the compound went into solution with the evolution of ammonia, and the alkaline solution on acidification gave 1-*indanone*-2-*glyoxylic acid*, m.p. 218°. (Found: C, 65.1; H, 4.2. $C_{11}H_8O_4$ requires C, 64.7; H, 3.9%). The acid was characterised by the preparation of the *quinoxalin derivative*, obtained in shining orange plates, m.p. 325°, by condensation with *o*-phenylenediamine. (Found: N, 10.8. $C_{17}H_{12}O_2N_2$ requires N, 10.1%). The compound dissolved in H_2SO_4 with a rose-red colour.

3-*Methyl*-4-*azafluorene*-1:2-*dicarboxylic Acid* (V).—The foregoing cyano-ester (III: 0.4 g.) was refluxed with aqueous alcoholic NaOH (30%, 6 c.c.) for 18 hours, filtered, alcohol removed in vacuum and the *acid* precipitated. The acid (0.2 g.) was obtained as a colorless crystalline mass, m.p. 269-71° from *iso*butanol. (Found: N, 5.2. $C_{15}H_{11}O_4N$ requires N, 5.2%).

3-*Methyl*-4-*azafluorene*.—An intimate mixture of dry lime and the dicarboxylic acid (V) was cautiously distilled and the reddish oily distillate was converted into the picrate, m.p. 212°, undepressed on admixture with an authentic specimen of the picrate.

2-*Cyano*-3-*methyl*-4-*azafluorene*-1-*carboxylic Acid* (IV).—The cyano-ester (III: 0.2 g.) was added to alcoholic NaOH (0.3 g. in 5 c.c. dry alcohol) and the mixture heated for 2 minutes. The *sodium salt* separating was collected, dissolved in water

and acidified. The *acid* was obtained as a gelatinous mass, turning granular on boiling with water. The compound was obtained in prismatic needles from *iso*butanol, m.p. 274·75°, yield 0.15 g. (Found: N, 11.7. $C_{15}H_{10}O_2N_2$ requires N, 11.2%). On thermal decarboxylation at 290° and collecting the product on a cold finger, 2-cyano-3-methyl-4-azafluorene was obtained, crystallising from alcohol in colorless needles, m.p. 183·84° (undepressed on admixture with the sample described before). (Found: N, 13.5. $C_{14}H_{10}N_2$ requires N, 13.6%).

Ethyl Acenaphthenone-glyoxylate.—A mixture of acenaphthenone (0.98 g.) and ethyl oxalate in dry alcohol (15 c.c.) was added to alcoholic sodium ethoxide (sodium 0.155 g., alcohol 5 c.c.). The dark mixture was left overnight in a refrigerator and worked up in the usual manner. The *ester* (0.95 g.) crystallised from alcohol in fine yellow crystalline powder, m.p. 100·101° (Duthie and Plant, *J. Chem. Soc.*, 1952, 1899, record m.p. 104°). (Found: C, 72.1; H, 4.6. Calc. for $C_{16}H_{12}O_4$: C, 71.6; H, 4.5%).

Ethyl 9-Cyano-8-methyl-7-azafluoranthene-10-carboxylate (VI: R = COOEt).—A mixture of the foregoing oxalyl derivative (0.4 g.) and 2-aminocrotononitrile (0.15 g.) in dry alcohol (5 c.c.) was set aside at the room temperature. The reactants slowly went into solution and the reddish material separating was collected after 14 days and crystallised from dilute alcohol. The *ester* (0.05 g.) was obtained as short prismatic needles, m.p. 144°. (Found: C, 76.7; H, 4.6. $C_{20}H_{14}O_2N_2$ requires C, 76.4; H, 4.5%).

Experiments on the Condensation of Ethyl 2-Aminocrotonate with 2-Hydroxymethylene-1-indanone.—(*i*). 2-Hydroxymethylene-1-indanone (9.5 g.) was dissolved in ethyl 2-aminocrotonate (25 g.) by warming on the steam-bath with the exclusion of moisture and then set aside at the room temperature for 4 days. The yellow material (2.7 g.) separating was collected and crystallised from benzene in light yellow prisms, m.p. 166°. (Found: C, 74.6, 73.0; H, 6.0, 6.1; N, 8.9, 9.0. $C_{20}H_{22}O_2N_2$ requires C, 74·5; H, 7.0; N, 8.7%). *I.R. spectrum*: $\lambda_{max.}^{nujol}$ 3.13s (NH bonded), 5.95 s (cyclic aromatic ketone), 6.07 s, 6.20 s, 6.53 s, 7.70 s and 8.70 m ($\rangle C-NH-C$)μ.

The compound imparted a greenish flourescence to H_2SO_4 and developed a dirty green colour with alcoholic ferric chloride. On warming with dilute alkali the compound went into solution with the evolution of ammonia and the alkaline solution on acidification regenerated the hydroxymethylene compound.

(*ii*). A mixture of the hydroxymethylene compound (3.2 g.) and ethyl 2-aminocrotonate (2.6 g.) was warmed on the water-bath till a homogeneous solution was obtained and then left at the room temperature for a week. The solid (0.4 g.) was collected and crystallised from *n*-butanol in yellow silky needles, m.p. 268°. This compound is also obtained when the above mentioned compound, m.p. 166°, is treated with dilute HCl or heated at 200° (evolution of ammonia). For analysis, the compound was dried at 80° for 2 hours in vacuum as it retained moisture tenaciously. (Found: C, 73.5; H, 5.2; N, 4.1. $C_{19}H_{19}O_3N$ requires C, 73 8; H, 6.2; N, 4.5%).

The compound exhibited a greenish red flourescence with H_2SO_4. On boiling the compound with alcoholic NaOH, steel-blue plates of the sodium salt of (VII) were obtained. These were collected, acidified and the solid crystallised from xylene

furnishing (VII), m.p. 233° (undepressed on admixture with an authentic specimen). (Found : C, 83.4 ; H, 4.9. Calc. for $C_{19}H_{14}O_2$: C, 83.2 ; H, 5.1%).

(*iii*). Equimolecular solutions of 2-hydroxymethylene-1-indanone and ethyl 2-aminocrotonate in dry alcohol were set aside at the room temperature for 15 days. Very fine yellowish crystals separating were crystallised from aqueous pyridine in light yellow prisms, m.p. 214°. (Found : C, 72.9, 72.8 ; H, 6.6, 6.2 ; N, 3.8%).

1-*Naphthylidene-acenaphthenone* (cf. Graeb and Jequier, *Annalen*, 1896, **290**, 204).—To a solution of acenaphthenone (0.5 g.) and 1-naphthaldehyde (0.45 g.) in alcohol (5 c.c.) two drops of NaOH solution (10%) were added. The mixture which darkened immediately was warmed for 15 minutes on the water-bath and left overnight at the room temperature. The *compound* (0.25 g.) crystallised from aqueous alcohol in thick prisms, m.p. 152-53°. (Found : C, 90.4 ; H, 4.7. $C_{23}H_{14}O$ requires C, 90.2 ; H, 4.6%).

p-*Tolylidene-acenaphthenone* was similarly prepared and obtained in yellow prismatic needles, m.p. 129-30° from aqueous alcohol (yield 75-85%). (Found : C, 89.0 ; H, 5.6. $C_{20}H_{14}O$ requires C, 88.9 ; H, 5.2%).

2-*Benzylidene-1-indanone* was prepared according to Mills and Akers (*loc. cit.*) with the aid of zinc chloride. The main product was different when alkaline catalysts were employed (Kipping, *J. Chem. Soc.*, 1894, **65**, 498). To a mixture of benzaldehyde (3.2 g.) and 1-indanone (4 g.) a few drops of alcoholic potash were added. The mixture soon acquired a creamy consistency. After agitating with a glass rod for 30 minutes, the mixture was triturated with alcohol, when a granular mass (4.8 g.) appeared. The compound is probably bis-*benzylidene-1-indanone*. It crystallised from acetic acid in colorless prisms, m.p. 238-40°. (Found : C, 85.8 ; H, 5.4 ; M.W., 333. $C_{25}H_{20}O_2$ requires C, 85.2 ; H, 5.7% ; M.W., 352). The *infra-red* spectrum showed a strong absorption at 5.95μ, indicating aromatic carbonyl group.

The *mono-oxime*, obtained on boiling with an excess of hydroxylamine hydrochloride in alcohol, crystallised from acetic acid in colorless rectangular plates, m.p. 284°. (Found : C, 82.3 ; H, 5.6 ; N, 3.2. $C_{25}H_{21}O_2N$ requires C, 81.7 ; H, 5.7 ; N, 3.8%). *Infra-red spectrum* : $\lambda_{max.}^{nujol}$ 2.9 s (OH), 6.0 s (aromatic ketone), 6.25 s (C=N)μ.

2-*Cyano-3-methyl 1-phenyl-4-azafluorene* (IX).—A mixture of 2-benzylidene-1-indanone (0.55 g.), 2-aminocrotononitrile (0.2 g.) and alcoholic sodium ethoxide (Na 0.06 g., alcohol 10 c.c.) was refluxed for 30 minutes, cooled and the *azafluorene* (0.1 g.) collected and crystallised from alcohol in colorless needles, m.p. 199°. (Found : C, 85.0 ; H, 5.0. $C_{20}H_{14}N_2$ requires C, 85.1 ; H, 5.0%).

9-*Cyano-8-methyl-10-phenyl-7-azafluoranthene*.—Benzylidene-acenaphthenone (1.25 g.) was condensed as above with 2-aminocrotononitrile (0.4 g.) in alcoholic sodium ethoxide (Na, 0.12 g. and alcohol, 15 c.c.). The mixture turned violet and within a few minutes a solid (0.75 g.) separated which was collected after 15 minutes. Crystallised from acetic acid, the *azafluoranthene* was obtained as yellowish needles, m.p. 209-10°. (Found : C, 87.2 ; H, 4.5 ; N, 8.2. $C_{23}H_{14}N_2$ requires C, 86.8 ; H, 4.4 ; N, 8.8%).

9-*Cyano*-8-*methyl*-10-p-*tolyl*-7-*azafluoranthene*, similarly prepared, crystallised from acetic acid in yellowish prismatic needles, m.p. 251-52°. (Found : C, 87.3 ; H, 5.1. $C_{24}H_{16}N_2$ requires C, 86.7 ; H, 4.8%).

9-*Cyano*-8-*methyl*-10-α-*naphthyl*-7-*azafluoranthene* was obtained as yellow prismatic needles from acetic acid, m.p. 263-65°. (Found : C, 88.7 ; H, 4.7. $C_{27}H_{16}N_2$ requires C, 88.0 ; H, 4.3%).

9-*Cyano*-10-*phenyl*-8-*hydroxy*-7-*azafluoranthene* (X).—Benzylidene-acenaphthenone (0.5 g.) and cyanoacetamide (0.16 g.) were added to sodium ethoxide (Na, 0.06 g. and alcohol, 15 c.c.). The mixture was warmed on the steam-bath for 15 minutes and then left for 3 days at the room temperature. The reddish product (0.25 g.) crystallised from acetic acid in light orange prisms, m.p. >320°. (Found : C, 82.9 ; H, 4.4. $C_{22}H_{12}ON_2$ requires C, 82.5 ; H, 3.8%).

8-*Keto*-9-*cyano*-10-*phenyl*-7 : 8 : 9 : 10 : 10a : 7a-*hexahydro*-7-*azafluoranthene* (XI).—The foregoing condensation was carried out with diethylamine as catalyst. The reaction mixture was left at 40° for 5 days. The *compound* separated in colorless plates, m.p. >320° from alcohol. (Found : N, 8.3. $C_{22}H_{16}O_2N_2$ requires N, 8.2%).

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CHEMICAL LABORATORY,
SCIENCE COLLEGE, PATNA-5.

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STUDIES IN DEHYDRATION OF CASTOR OIL

By V. A. Saraf and K. K. Dole

(A) Anthraquinone-1-sulphonic acid, (B) anthraquinone-2-sulphonic acid, (C) *p*-toluene-thiosulphonic acid, (D) metanilic acid, (E) methyl benzenesulphonate, (F) ethyl benzenesulphonate and (G) ethyl toluene-*p*-sulphonate have been studied with respect to their catalytic action in the dehydration of castor oil. (A) and (B) have been found as active dehydrating catalysts. The position of $-SO_3H$ group has very little influence on their catalytic activities. *p*-Toluene-thiosulphonic acid is found to be a useful dehydrating catalyst at 280°. Metanilic acid is found to be less active as a dehydrating catalyst.

The three esters of sulphonic acids are less active at 250°, but their activity increases at 280°. Esters of sulphonic acids reduce the hydrolysis of the oil to a certain extent and improve the colour of the dehydrated samples.

Sulphonic acids and their derivatives have shown considerable promise in dehydrating castor oil. A number of sulphonic acids having different substituent groups in the aromatic nucleus have already been studied by Dole and Keskar (*Proc. Ind. Acad. Sci.*, 1953, **38A**, 135.). In the present investigation a few sulphonic acids and esters of sulphonic acids have been successfully employed for the dehydration of castor oil.

Experimental

Dehydration of castor oil was carried out under atmospheric pressure (~713 mm of Hg) and under reduced pressure (20 mm of Hg). The experimental and analytical procedures followed in this investigation are the same as described by Dole and Keskar (*loc. cit.*).

Table I

Values of samples dehydrated at 713 mm pressure.

		Conc. of catalyst.	Dehydration Temp.	Time.	I. V.*	H. V.	A. V.	M.W.†	R. I.**	Colour B.	R.	Y.
1.	Anthraquinone--1-sulphonic acid	0.1%	250°	50 min.	145.5	38.3	10.0	1032	1.4762	1	12	12
2.	Anthraquinone--2-sulphonic acid	0 1	250°	50	145.8	37 6	10 1	1030	1.4790	1	12	13
3.	*p*-Toluene-thio--sulphonic acid	0.5	280°	50	147.2	19.4	11.3	1092	1.4795		...	
4.	Metanilic acid	1.0	290°	60	118.7	86.9	7.5	...	...	6	18	10.1
5.	Methyl benzene--sulphonate	0.2	280°	50	150.1	7.5	26.2	1151	1.4805		...	
6.	Ethyl benzene--sulphonate	0 2	280°	50	149.1	18.7	26.7	958.3	1.4805		...	
7.	Ethyl toluene--*p*-sulphonate	0 4	280°	40	146.2	23.1	26.9	996.8	1.4780	0	5.1	10 1

* Iodine value by the Wöburn method at room temperature (27-28°.).

† By cryoscopic method using benzene, special for molecular weights.

** Refractive index by Abbe's refractometer at 40°.

Colour: By Lovibond tintometer using 10 mm cell : B - Blue ; R - Red ; Y - Yellow.

H.V. = hydroxyl value ; A.V. = acid value.

TABLE II

Rate of dehydration of castor oil at 713 mm pressure.

No.	Catalyst	Conc. of catalyst.	Temp. of dehydration.	Iodine values of samples drawn at intervals (mins.) of 10.	20	30.	40.	50.
1.	Anthraquinone--1-sulphonic acid	0.1%	250°	116.2	128.8	136.1	142.7	145.5
2.	Anthraquinone--2-sulphonic acid	0.1	250°	123.6	132.4	143.3	146.2	146.8
3.	*p*-Toluene thio--sulphonic acid	0.5	280°	122.6	131.0	138.6	142.5	147.2
4.	Methyl benzene--sulphonate	0.2	280°	126.6	136.2	143.5	145.5	150.1
5.	Ethyl benzene--sulphonate	0.2	280°	125.2	134.7	142.0	144.6	149.1
6.	Ethyl toluene--*p*-sulphonate	0.4	280°	118.4	134.5	144.5	146.2	144.5

TABLE III

Values of samples dehydrated at 20 mm pressure.

No.	Time of dehydration.	I.V. (Wobum)	H.V.	A.V.	M.W.	R.I. (40°)	Colour. B.	R.	Y.
1.	50 min.	139.9	27.9	4.9	1018	1.4760	0	2	15
2.	60	141.7	25.6	4.8	1019	...	1	3	17
3.	50	144.4	21.2	6.8	1125	1.4782	0	1	4
4.	50	148.1	10.4	5.3	1055	1.4739	1.9	3	9
5.	50	145.8	24.2	4.5	...	...	1	1.5	5
6.	40	137.2	20.7	4.4	1059	1.4765	0	1.2	10

No. of catalysts, concentration and dehydration temp. are the same as in Table II.

DISCUSSION

Effect of Substitution of Different Groups in Sulphonic Acids.—Dole and Keskar (*loc. cit.*) represented sulphonic acids by the general formula $X\text{-}SO_2\text{-}OH$, wherein "X" was an alkyl (or substituted alkyl) or aryl (or substituted aryl) radical. The change in the X-part of the molecule was observed to change the properties of the catalyst to a great extent.

In the case of anthraquinone-sulphonic acids (both 1- and 2-), the dehydration is nearly complete with 0.1% of the catalyst at 250° in about one hour. As compared with benzenesulphonic acid, the acid values of the dehydrated samples are less. With the 1-acid, it is 10.0 and with 2-acid, it is 10.1. It seems therefore that the reaction of hydrolysis is suppressed appreciably. The position of the $-SO_3H$ group has practically little influence on the acitivity of the catalysts. *p*-Toluene-thiosulphonic acid is found to be an active catalyst at 280°. However, the percentage of the acid required to dehydrate the oil is more, viz., 0.5 %, when compared with *p*-toluenesulphonic acid, viz., 0.3% (*loc. cit.*). It is seen from the rates of dehydration with *p*-toluenesulphonic acid and *p*-toluene-thiosulphonic acid as catalysts that the former is more active than the latter.

Metanilic acid is found inactive as a dehydrating catalyst. This retarding action of the $-NH_2$ group was also observed by Dole and Keskar (*loc. cit.*).

Esters of Sulphonic Acids.—The esters of sulphonic acids are found to be active, but unlike the free sulphonic acids, they are less active at 250°. When the temperature of dehydration is increased to 280°, the reaction becomes rapid. The reactivity of the esters may be due to their hydrolysis into free sulphonic acids. It may also be assumed that the esters react by way of rupture of the alkyl-oxygen linkage (Ferns and Lapworth, *J. Chem. Soc.*, 1912, **101**, 273; Philips, *ibid.*, 1923, **123**, 44). when the reactivity of the esters is compared with the corresponding free acids, it is observed that (*i*) esters are less active than free acids, (*ii*)in the case of esters, hydrolytic reaction is less, and (*iii*) comparatively pale coloured dehydrated products are obtained. Moreover, the activities of methyl and and ethyl esters are similar.

From the above observations, it is probable that only a part of the ester breaks up into free acid, which is supposed to be responsible for the catalytic reaction.

CHEMISTRY DEPARTMENT,
FERGUSSON COLLEGE,
POONA-4.

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DEHYDRATION OF CASTOR OIL BY PHENOL-SUBSTITUTED SULPHONIC ACIDS AND THEIR POTASSIUM SALTS

BY V. A SARAF AND K. K. DOLE

Among several phenol-substituted sulphonic acids and their salts, employed as dehyd.ating catalysts in dehydration of castor oil, *p*-phenol-, *m*-cresol- and resorcinol-sulphonic acids have been found to be active at 250°; potassium salts of *p*-phenol- and *m*-cresol-sulphonic acids are active both under atmospheric pressure and under reduced pressure; potassium guaiacol-sulphonate is found to be active under atmospheric pressure. Phosphoric acid, sodium dihydrogen phosphate and ammonium dihydrogen phosphate have also been studied as catalysts; among the three, phosphoric acid is found to be a good catalyst, and is reactive at 280° and affords exceptionally pale coloured dehydrated product with low acid value. The other two are found to be inactive.

The use of different naphthol-sulphonic acids as catalysts for dehydration of castor oil was reported by Walton, Coffey and Knapp (*Chem. Abs.*, 1948, **42**, 6557). They claimed that 2-naphthol-6-sulphonic acid afforded 100% dehydration of the oil at 260° in one hour with less amount of decomposition of the oil. Dole and Keskar (*Proc. Ind. Acad. Sci.*, 1953, **38A**, 135) also found phenol-sulphonic acid to be a useful dehydrating catalyst and observed that the introduction of -OH group in the benzenesulphonic acid mitigated the tendency of decomposition of the oil without affecting the dehydrating capacity of the catalyst. As a consequence, phenol-sulphonic acid gave paler products than benzenesulphonic acid. Potassium salt of phenol-sulphonic acid was also studied and reported by them to be a good dehydrating catalyst.

In view of the above encouraging results, the use of some more phenol-substituted sulphonic acids as catalysts has been studied in the present investigation.

Phenol-substituted free sulphonic acids were quite active at 250°. The dehydration was rapid at 270° in the case of the potassium salts of phenol-sulphonic acids. The dehydration was therefore carried out at 250° in the former case and at 270° in the latter. When *m*-cresol-sulphonic acid, *p*-phenol-sulphonic acid, salts of *p*-phenol-sulphonic, *m*-cresol-sulphonic and guaiacol-sulphonic acids were used as catalysts, the period of dehydration was one hour. In the remaining catalysts, the period of dehydration was 50 minutes.

It was observed that phosphoric acid was less active at 250°, but its activity increased when dehydrated at 280°. The acid salts of phosphoric acid, viz., sodium dihydrogen phosphate and ammonium dihydrogen phosphate, were found to be inactive even when 5.0% of each was employed for dehydration.

EXPERIMENTAL

The dehydration reaction was carried out under atmospheric pressure (near about 713 mm of mercury) and under vacuum (20 mm of mercury). The experimental and analytical procedures adopted in this investigation are the same as described before (Dole and Keskar, *loc. cit.*).

TABLE I

Values of samples dehydrated with phenol-substituted sulphonic acids and their potassium salts as catalysts.

No.	Catalyst	Pressure.	Conc. of catalyst.	I. V.	H. V.	A. V.	M. W.	R. I.	Colour, B. R. Y.
1.	Resorcinol-sulphonic acid	713 mm	0.3%	138 3	49.6	4.3	976.3	1.4780	1 14 11
	Do	20	0.3	155.7	...	2 0	925 5	1.4790	0 10 18
2.	*m*-Cresol-sulphonic acid	713	0.4	142.7	44.1	4.0	1101	1.4770	... ...
	Do	20	0.4	155.1	29 7	1.8	913.0	1.4705	... ...
3.	2-Naphthol-1-sulphonic acid	713	0.3	204.1	125.9	5.1	...	...	.. ..
4.	2 :4-Dinitro-1-naphthol-7-sulphonic acid	713	0.1	107.0	105.5	4.2	982.8	1.4735	... ...
5.	*p*-Phenol-sulphonic acid	713	0.3	131.3	55.7	6.0	967.9	1.4765	... ...
6.	K *p*-phenol-sulphonate	713	3.0	150 5	29 7	6.8	969.0	1.4775	... ...
	Do	20	3.0	156 4	16.5	8.7	879 0	1.4780	... ...
7.	K *m*-cresol-sulphonate	713	2.0	148.8	44.3	5.0	1001	1.4780	... ...
	Do	20	2.0	164.1	21.2	3 1	944.0	1.4795	... ...
8.	K guaiacol-sulphonate	713	2.0	147.5	35.2	3.6	1001	1.4800	1.0 2.3 12
	Do	20	2.0	90.0	154.0	...	...	...	... ...

I. V. : Iodine value by Wöburn method at room temperature (27°-28°).

H. V. = hydroxyl value; A. V. = acid value; M. W = Molecular weight by cryoscopic method using benzene, special for molecular weights.

R. I. = Refractive index by Abbe's refractomer at 40°.

Colour : By Lovibond tintometer using 10 mm. cell; B-Blue; R-Red; Y-yellow.

TABLE II

Rate of dehydration of castor oil.

No.	Catalyst.	Conc. of catalyst.	I. V. of samples drawn at intervals (in mins.) of 10.	15.	20.	30.	40.	45.	50.	60.
1.	Resorcinol-sulphonic acid.	0.3%	130.7	...	136.2	138.0	138.4	...	138.3	...
2.	*m*-Cresol-sulphonic acid	0.4	136.1	...	140.3	141.6	142.3	...	142.5	142.7
3.	*p*-Phenol-sulphonic acid	0.1	97.1	...	100.4	103.0	104.0	...	107.0	...
4.	K *m*-cresol-sulphonate	2.0	...	132.1	...	141.4	...	148.6	...	148.8
5.	K guaiacol-sulphonate	2.0	122.4	...	136.1	143.2	146.9	...	147.1	147.5

TABLE III

Physical and chemical characteristics of the dehydrated castor oil samples.

Conc of phosphoric acid = 0 3%.
Temp. of dehydration = 280° ± 5°.
Time of dehydration = 60 minutes.

	At 713 mm.	At 20 mm.			At 713 mm.	At 20 mm.
I. V. (Wöburn)	151.5	147.8	Ref. index at 40°		1.4800	1.4815
Hydroxyl value	23.5	23.7	M. W.		877.6	899.1
Acid value	11.2	6.4	Colour :	B	0.0	0 0
Sapon. value	194.7	182.1		R	1.1	0.4
				Y	10.0	0.8

DISCUSSION

Phenol-substituted sulphonic acids are active dehydrating catalysts. They furnish paler products than benzenesulphonic acid.

Due to the high temperature of the dehydration reaction the decomposition of the oil is rapid. The decomposition products produced at the temperature of reaction may be oxidised, and may thus cause the dark colour of dehydrated samples. In the case of phenol-substituted sulphonic acids, the oxidation of the decomposition products is checked to a great extent, due evidently to the antioxidant property of phenols.

It is observed that dehydrated castor oil is sensitive to antioxidants (Ijak, *Chem. Paint*, 1951, **14**, 188). Thus, the improvement in the colour of the dehydrated products, when hydroxy-substituted aromatic sulphonic acids are used as catalysts, may be due to their inhibiting influence on this oxidation of the oil and the decomposition products.

The potassium salts of phenolic sulphonic acids are active due to their slightly acidic character of the salts. Thus, potassium salts of *m*-cresol-sulphonic and *p*-phenol-sulpho-

nic acids are active both under atmospheric and reduced pressures. Potassium guaiacol-sulphonate is, however, found to be active only under atmospheric pressure.

Phosphoric acid is also found to be an active dehydrating catalyst. It gives paler products than benzenesulphonic acid. Under reduced pressure, the dehydrated sample has an exceptionally pale colour and low acid number. In this case also it may be surmised that, like phenol-substituted sulphonic acids, the oxidation of the decomposition products is retarded to a great extent, and the antioxidant property of phosphoric acid (Bailey, "The Retardation of Chemical Reactions", 1937, Edward Arnold and Co. London, p. 118) may be the cause for this improvement in colour.

CHEMISTRY DEPARTMENT,
FERGUSSON COLLEGE,
POONA. 4

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HYDROLYSIS OF LEAD^{II} AND ITS EFFECT ON THE SOLUBILITY OF LEAD IODATE

By R. N. Misra and S. Pani

Sn^{II} and Pb^{II} are found to be more hydrolysed in aqueous solution than some other divalent ions of comparatively smaller radii. The hydrolysis in some cases depends on the capacity of the cation to form cova'ent bond, besides on charge and radius. The hydrolysis of divalent lead ion might be represented by,

$$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+ \quad \ldots (1)$$

and

$$PbOH^+ + H_2O \rightleftharpoons Pb(OH)_2 + H^+ \quad \ldots (2)$$

taking place in two steps. The extent of hydrolysis depends on the activity of water, and therefore expected to be appreciable in very dilute solution of lead salts. In a saturated aqueous solution of lead iodate, the hydrolysis is found to be appreciable and $4S^3$ (where S is the solubility of lead iodate in g. mole per litre at a given ionic strength at 35°) does not represent the solubility product of lead iodate. $4S^3$ is equal to $K_s \times [H^+] + K_s \times k$ (where K_s is a constant, k is the equilibrium constant of the reaction (1) and $[H^+]$ is the molar concentration of hydrogen ion). Hence $4S^3$ at lower p_H is hydrogen-dependent, whereas at higher p_H, the factor $K_s \times [H^+]$ being smaller compared to $K_s \cdot k_1$, it is independent of p_H. The mean value of k is 0.121.

The Pb^{2+} ion with ionic radius of 1.21Å, which is greater than those of Ca^{2+} (0.99Å) and Sr^{2+} (1.13Å), is known to hydrolyse in aqueous solution to an appreciable extent, giving rise to basic salts, many of which have been isolated in the free state. This shows that the charge/radius ratio is not the only factor that can account for the electrical character or the electronegativity of the element or its ions. The electronic structure and the position of the element in the Periodic Table are primarily responsible for electron affinity and electronegativity of the elements. It is only in the case of similar elements of the same vertical group in the Periodic Table that charge/radius ratio determines their relative electrochemical behaviour. Many of the inorganic lead compounds therefore show covalent character, particularly the halides and the oxides. Standing just above hydrogen in the electropotential series of elements, lead shows rather a weak electropositive character and behaves as an amphoteric element. Such elements, when occur as positive ion, tend to attract electrons from other groups or molecules, giving rise to the formation of complexes. Pb^{2+} in aqueous solution therefore tends to attract and hold around itself one or more water molecules, and thereby suffer hydrolysis.

The hydrolysis of Pb^{2+} can be assumed to be taking place in two steps, as represented below.

$$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+ \quad \ldots \quad \ldots (1)$$

$$PbOH^+ + H_2O \rightleftharpoons Pb(OH)_2 + H^+ \quad \ldots \quad \ldots (2)$$

The hydrolysis, being dependent on the activity of water, is expected to be high in very dilute solutions of lead salts. In a saturated solution of sparingly soluble salt therefore, the hydrolysis would be appreciable. The hydrolysis of lead sulphate solution

has been observed previously (Pleissner, *Arb. Kaiser. Ges. Amt.*, 1907, **26**, 419; Sehnal, *Compt. rend.*, 1909, **148**, 1394). Recently, hydrolysis of mercurous chloride in aqueous solution has been reported (Dry and Gledhill, *Trans. Faraday Soc.*, 1955, **51**, 1119).

If lead ion hydrolyses, as suggested above, in a saturated aqueous solution of lead iodate, the concentration of lead ion would be p_H-dependent, besides depending on the concentration of iodate ion. The solubility would change with p_H. To verify this the solubility of lead iodate in perchloric acid of different concentrations was determined. It was, however, assumed that perchlorate and iodate ions did not form complex with lead.

Experimental

Lead iodate was prepared after La Mer and Goldman (*J. Amer. Chem. Soc.*, 1930, **52**, 2791). Chemicals used were of G. R. quality. Perchloric acid and sodium perchlorate used were prepared from 70% perchloric acid. The solubilities were measured at $35° \pm 0.2°$. The same sample of lead iodate was used throughout the investigation. The solubilities of lead iodate in (1) sodium perchlorate solution of different concentrations (0.3 – 0.02 *M*), (2) perchloric acid solution of the same concentration as sodium perchlorate, (3) mixture of sodium perchlorate and perchloric acid of the same ionic strength and (4) mixture of perchloric acid and potassium iodate were determined. The results are shown in Tables Ia, Ib, Ic and Id respectively, where *S* represents the solubility in g. moles of lead iodate per litre. The concentrations in g. moles per litre are expressed by square brackets.

Table Ia

In $NaClO_4$.

$[NaClO_4]$.	$S \times 10^5$.
0.30	9.860
0.25	9.520
0.20	9.175
0.18	9.005
0.16	8.660
0.14	8.485
0.12	8.230
0.10	8.060
0.08	7.720
0.06	7.205
0.04	6.860
0.02	6.515
0.00	5.085

Table Ib

In $HClO_4$.

$[HClO_4]$.	$S \times 10^5$.
0.30	15.17
0.25	13.95
0.20	12.73
0.18	12.02
0.16	11.50
0.14	10.98
0.12	10.37
0.10	9.590
0.08	8.980
0.06	8.865
0.04	7.495
0.02	6.530
0.00	5.085

Table Ic

In mixture of $NaClO_4$ *and* $HClO_4$.

$[HClO_4]$.	$[NaClO_4]$.	$S \times 10^5$.
0.30	0.00	15 17
0.25	0.05	14.23
0.20	0.10	13.43
0.18	0.12	12 90
0.16	0.14	12.64
0.14	0.16	12.21
0.12	0.18	11.86
0.10	0.20	11.51
0.08	0.22	11.16
0 06	0.24	10.72
0.04	0.26	10.37
0.02	0.28	9.86

TABLE Id

Solubility in mixture of $HClO_4$ *and* KIO_3.

$[HClO_4]$.	$[KIO_3]\times10^5$.	$S\times10^5$.	$S\times[IO_3^-]^2\times10^{12}$.
0.20	0.00	12.73	8.250
0.20	6.667	10.87	8.835
0.20	8.000	10.47	8.974
0.20	9.333	10.14	8.888
0.20	10.67	9.555	8.476
0.20	12.00	9.315	8.736
0.20	13.33	8.910	8.648
0.20	16.63	8.115	8 764

TABLE II

Ionic strength = 0.30

$[H^+]$.	$[PbOH^+]\times10^5$.	$[Pb^{2+}]\times10^5$.	k_1.
0.30	4.157	11.010	0.113
0.25	4.316	9.914	0.109
0.20	4.854	8.585	0.113
0 18	5.252	7.648	0.124
0.16	5.469	7.171	0.122
0.14	5.862	6.348	0,129
0.12	6.213	5.647	0.132
0.10	6.595	4.915	0.134
0.08	7.020	4.140	0.136
0 06	7 608	3.112	0.146
0.04	8.127	2 243	0.145

TABLE III

Ionic strength.	$[H^+]$.	$[PbOH^+]\times10^5$.	$[Pb^{2+}]\times10^5$.	k_1.
0.30	0 30	4.157	11.010	0 113
0.25	0.25	4.432	9.518	0.116
0.20	0.20	4.766	7.964	0.120
0.18	0.18	4.903	7 297	0.121
0.16	0.16	4.910	6.590	0.119
0.14	0.14	5.093	5 887	0.121
0.12	0.12	5.183	5.187	0.120
0.10	0.10	5.693	3.879	0.146
0.08	0.08	5.705	3.274	0.139

TABLE IV

Ionic strength = 0.20. $[H^+]$ = 0.20.

$[PbOH^+]\times10^5$.	$[Pb^{2+}]\times10^5$.	k_1.
4.766	7.964	0.120
3.827	7.043	0.109
3.691	6.769	0.109
3.525	6.615	0 107
3.482	6.073	0.115
3.294	6.021	0 109
3 184	5.726	0.111
2 861	5.254	0.109

DISCUSSION

The increase in the solubility of lead iodate with increasing concentration of sodium perchlorate is most probably due to the increasing ionic strength since an increase in the solubility of a similar order with the increasing ionic strength is observed in the solubility of barium iodate in potassium chloride, nitrate, chlorate and perchlorate solutions (Seidell, "Solubitities of Inorganic and Metal Organic Compounds", 3rd. Ed., 1940, Vol. I, p. 168). The solubility in perchloric acid is, however, higher than that in sodium perchlorate of the same ionic strength. This might be due to some reaction involving hydrogen ion. This is further confirmed by the solubilities in mixtures of sodium perchlorate and perchloric acid of constant ionic strength (the concentration of lead iodate being small, its contribution to the ionic strength is neglected). The solubility increases with increasing cencentration of hydrogen ion. The activity coefficients are taken to be constant at constant ionic strength. It is assumed that the solubility product ($4S^3$) is directly proportional to the nth power of the concentration of H^+ ion. Hence,

$$4S^3 = K\times[H^+]^n \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

Taking logarithm to the base 10,

$$\log 4 + 3 \log S = \log K + n \log [H^+] \quad \ldots \quad \ldots \quad (3\text{-}1)$$

or

$$3 \log S = \log K_1 + n \log [H^+] \quad \ldots \quad \ldots \quad (3\text{-}2)$$

$$3pS = p K_1 + n p_H \quad \ldots \quad \ldots \quad \ldots \quad (3\text{-}3)$$

The solubilities in the mixture of sodium perchlorate and perchloric acid of constant ionic strength were used. The concentration of hydrogen ion was taken to be equal to the concentration of perchloric acid. In Fig. 1, $3\,pS$ is plotted against p_H. The plot is a smooth curve with changing slope. The slope at lower p_H is 1, whereas at higher p_H, it approaches zero. $4S^3$ is proportional to the concentration of hydrogen ion at lower p_H, but is independent of it at higher p_H. Strictly speaking, $4S^3$ does not represent the solubility product of lead iodate.

FIG. 1

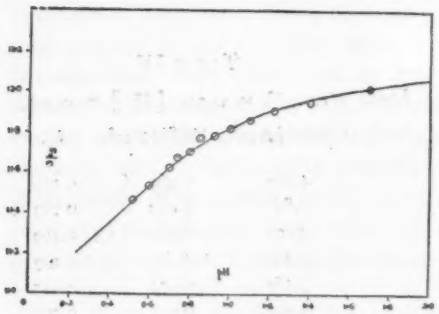
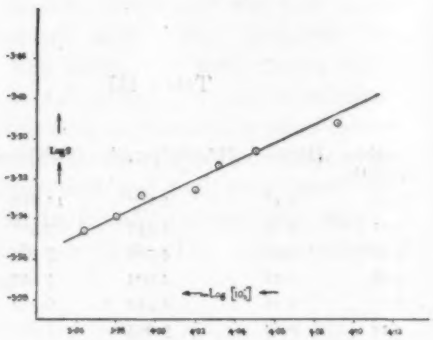


FIG. 2



The p_H and ionic strength of the saturated solution of lead iodate in 0.2*M*-$HClO_4$ containing a small amount of KIO_3 can be taken as constant. The solubility decreases with increasing concentration of iodate ion. It is assumed that the solubility of lead iodate is inversely proportional to the *mth* power of the concentration of iodate ion at constant H^+-ion concentration. Hence,

$$S \times [IO_3^-]^m = K_2 \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

Taking logarithm to the base 10

$$\log S = \log K_2 - m \log [IO_3^-] \quad \ldots \quad \ldots \quad (4\text{-}1)$$

In Fig. 2 $\log S$ is plotted against $-\log [IO_3^-]$; the plot is a straight line with the slope equal to 2. At constant p_H therefore S, *i.e.* total lead in the solution, is inversely proportional to the square of the concentration of iodate ion. (The value of $S \times [IO_3^-]^2$ is given in the last column of Table ID and is fairly constant).

$$S \times [IO_3^-]^2 = K_2 \quad \ldots \quad \ldots \quad \ldots \quad (4\text{-}2)$$

If no potassium iodate be added, $[IO_3^-] = 2S$, and

$$4 S^3 = K_2 \quad \ldots \quad \ldots \quad \ldots \quad (4\text{-}3)$$

The above equation (4-3) holds good at constant p_H. The relationship between total lead and iodate ion confirms the assumption that no iodate complex of lead is formed at the concentration of iodate ion of the order of the solubility of lead iodate.

The changes in the solubility and in the value of $4S^3$ with change in p_H are most probably due to hydrolysis of lead ion, as represented by equations (1) and (2). The equilibrium constants at a given ionic strength may be represented by equation (1-1) and (2-1) respectively.

$$\frac{[Pb\,OH^+] \times [H^+]}{[Pb^{2+}]} = k_1 \quad \ldots \quad \ldots \quad (1\text{-}1)$$

$$\frac{[Pb(OH)_2] \times [H^+]}{[PbOH^+]} = k_2 \quad \ldots \quad \ldots \quad (2\text{-}1)$$

The total lead in the solution [Pb] (is equal to S) is given by

$$[Pb] = [Pb^{2+}] + [PbOH^+] + [Pb(OH)_2] \quad \ldots \quad (7)$$

$$= [Pb^{2+}]\left(1 + \frac{k_1}{[H^+]} + \frac{k_1 \times k_2}{[H^+]^2}\right) \quad \ldots \quad \ldots \quad (7\text{-}1)$$

If the second hydrolysis is assumed to have taken place to a small extent, compared to first, the concentration of $Pb(OH)_2$ would be small and may be neglected. Hence,

$$[Pb] = [Pb^{2+}] \times \left(1 + \frac{k_1}{[H^+]}\right) \quad \ldots \quad \ldots \quad (7\text{-}2)$$

or

$$S = [Pb^{2+}]\left(1 + \frac{k_1}{[H^+]}\right) \quad \ldots \quad \ldots \quad (7\text{-}3)$$

The above equation indicates that (*i*) when total lead, *i. e.* iodate ion, is constant $[Pb^{2+}]$ varies with the concentration of hydrogen ion, and (*ii*) when the concentration of hydrogen ion is constant, $[Pb^{2+}]$ is directly proportional to the total lead. It has been shown before that at constant p_H, S, *i.e.* total lead, is inversely proportional to the square of the concentration of iodate ion ; the same relationship is thereefore true of lead ion. It follows therefore that

$$\frac{[Pb^{2+}] \times [IO_3^-]^2}{[H^+]} = K_s \quad \ldots \quad \ldots \quad \ldots \quad (8)$$

where K_s is a constant.

$4S^3$ is actually the product of the concentration of total lead and the square of the concentration of iodate ion.

$$4S^3 = [Pb] \times [IO_3^-]^2 \quad \ldots \quad \ldots \quad \ldots \quad (9)$$

$$= [Pb^{2+}] \times \left(1 + \frac{k_1}{[H^+]}\right) \times [IO_3^-]^2 \quad \ldots \quad \ldots \quad (9\text{-}1)$$

$$= K_s \times [H^+] \times \left(1 + \frac{k_1}{[H^+]}\right) \quad \ldots \quad \ldots \quad (9\text{-}2)$$

or

$$4S^3 = K_s \times [H^+] + K_s \times k_1 \quad \ldots \quad \ldots \quad \ldots \quad (9\text{-}3)$$

$4S^3$ is the sum of a p_H-dependent and a constant term and it is directly proportional to the concentration of H^+.

When p_H is high and k_1 is greater than $[H^+]$, the p_H-dependent term, $K_s \times [H^+]$, becomes small and $4S^3$ is given by $K^s \times k_1$. The equation (9-3) satisfactorily explains the experimental curve in Fig. 1 and confirms the assumption that the second hydrolysis of lead ion has taken place to a very small extent.

The p_H-dependent term would be small and therefore negligible in the neutral solution. The term $K_s k_1$, which is constant, is equal to $4S_0^3$, where S_0 is the solubility of lead iodate in sodium perchlorate solution of the same ionic strength. The equation (9-3) therefore reduces to

$$4S^3 = K_s' [H^+] + 4S_0^3 \quad \ldots \quad \ldots \quad \ldots \quad (10)$$

or

$$4S^3 - 4S_0^3 = K_s[H^+] \quad \ldots \quad \ldots \quad \ldots \quad (10\text{-}1)$$

or

$$4S^3 - 4S_0^3 = [Pb^{2+}] \times [IO_3^-]^2 \quad \ldots \quad \ldots \quad (10\text{-}2)$$

$[IO_3^-]$ being equal to $2S$,

$$\frac{4S^3 - 4S_0^3}{4S^2} = [Pb^{2+}] \quad \ldots \quad \ldots \quad \ldots \quad (10\text{-}3)$$

or

$$S - (S_0^3/S^2) = [Pb^{2+}] \quad \ldots \quad \ldots \quad (10\text{-}4)$$

$[Pb^{2+}] + [PbOH^+] = S$, hence,

$$S_0^3/S^2 = [PbOH^+] \quad \ldots \quad \ldots \quad \ldots \quad (10\text{-}5)$$

The concentration of $PbOH^+$ is calculated by equation (10-5). The concentration of lead ion is obtained by subtracting $[PbOH^+]$ from S, the solubility of lead iodate in perchloric acid or mixture of perchloric acid and sodium perchlorate of a given ionic strength. The concentration of hydrogen ion is taken to be equal to the concentration of perchloric acid. k_1, calculated by equation (1-1), is given below. The results obtained from (*i*) the solubility in 0.3*M*-$NaClO_4$ (S_0) and those in $NaClO_4$ and $HClO_4$ of the same ionic strength (S), (*ii*) the solubility in $NaClO_4$ (S_0) and those in $HClO_4$ of the same concentration (S) and that in 0.2*M*-$NaClO_4$ (S_0) and those in 0.2M-$HClO_4$ containing very small amount of KIO_3 (S) are recorded in TablesI I-IV respectively. k_1 is fairly constant and the mean value is 0.121. k_1 can also be obtained graphically. If $4S^3$ is plotted against $[H^+]$, the equation (9-3) indicates that a straight line would be obtained, the slope of which would give the value of K_s and the intercept, that of $K_s \times k_1$. The solubilities in the mixtures of sodium perchlorate and perchloric acid (constant ionic strength) were used. Most of the points lie very close to a straight line. The slope is 3.0×10^{-11} and the intercept is 3.3×10^{-12}. k_1 is therefore 0.11. This is in agreement with the calculated value.

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DEPARTMENT OF CHEMISTRY,
RAVENSHAW COLLEGE,
CUTTACK-3. ORISSA.

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NITRATO-LEAD^{II} COMPLEX AND HYDROLYSIS OF LEAD^{II} IN AQUEOUS SOLUTION

By R. N. Misra and S. Pani

The same type of solubility as observed in the previous communication (this *issue*, p. 387) has also been observed in nitric acid and in sodium nitrate solutions. The solubilities in sodium nitrate and nitric acid are respectively greater than those in sodium perchlorate and perchloric acid of the same ionic strength. The latter observation is probably due to the formation of nitrato-lead complex. In neutral solution (in saturated solution of lead iodate in sodium nitrate) the complex mostly consists of hydroxo-nitrato-lead complex, $PbOH.NO_3$, whereas in acid solution this complex together with nitrato-lead complex, $PbNO_3^+$, exist. The equilibrium constants of the reactions:

$$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+ \quad \ldots \quad \ldots \quad (1)$$
$$Pb^{2+} + NO_3^- \rightleftharpoons Pb\,NO_3^+ \quad \ldots \quad \ldots \quad (2)$$
$$PbOH^+ + NO_3^- \rightleftharpoons PbOHNO_3 \quad \ldots \quad \ldots \quad (3)$$
$$PbNO_3^+ + H_2O \rightleftharpoons PbOH\,NO_3 + H^+ \quad \ldots \quad \ldots \quad (4)$$

have been determined and are 0.161, 3.83, 4.94 and 0.186 respectively.

The existence of nitrato-lead complex $PbNO_3^+$ has been reported by several workers (Righellato and Davies, *Trans. Faraday Soc.*, 1930, **26**, 592; Plake, *Z. physikal. Chem.*, 1932, **A162**, 257) Zikler, *ibid.*, 1932, **A163**, 1; Nasanen, *Ann. Acad. Sci. Fennicase, AII Chem.*, 1945, No. 13, 1; Hershenson, Smith and Hume, *J. Amer. Chem. Soc.*, 1953, **75**, 508). The equilibrium constant of the reaction

$$Pb^{2+} + NO_3^- \rightleftharpoons PbNO_3^+ \quad \ldots \quad \ldots \quad (1)$$

has been found to lie between 1.6 and 15. This difference in the equilibrium constant might be accounted for as due to different experimental conditions. This, however, does not lead to the actual factor responsible for this variation. Further investigation was thought to be necessary. The authors in the previous paper (this *issue*, p. 387) have discussed the effect of the variation of the concentration of hydrogen ion on the solubility of lead iodate. It has been shown that in a saturated solution of lead iodate in perchloric acid solution, the product of the concentration of lead ion and the square of the concentration of iodate ion is not constant at all p_H, but directly proportional to the concentration of H^+.

$$\frac{[Pb^{2+}] \times [IO_3^-]^2}{[H^+]} = K_s \quad \ldots \quad \ldots \quad (2)^*$$

They have further shown that

$$4S^3 = K_s \times [H^+] + K_s \times k_1 \quad \ldots \quad \ldots \quad (3)\dagger$$

where k_1 is the first hydrolysis constant, that is the equilibrium constant of the reaction,

$$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+ \quad \ldots \quad (4)$$
$$\frac{[PbOH^+] \times [H^+]}{[Pb^{2+}]} = k_1 \quad \ldots \quad \ldots \quad (5)$$

* Eq. (8) in the previous paper (*loc.cit.*)
† Eq. (9-3) in the previous paper (*loc.cit.*)

In the neutral solution (saturated solution of lead iodate in sodium perchlorate solution) the concentration of hydrogen ion being small, the factor $K_s \times [H^+]$ in equation (3) is small, and hence,

$$4S_o^3 = K_s \times k_1, \quad \ldots \quad \ldots \quad (6)$$

where S_o is the solubility of lead iodate in sodium perchlorate solution. Substituting the value of K_s and k_1 from equations (2) and (5) respectively, the equation (6) can be written as

$$4S_o^3 = [PbOH^+] \times [IO_3^-]^2 = K_s \times k_1 \quad \ldots \quad (7)$$

The product of the concentration of $PbOH^+$ ion and the square of the concentration of iodate ion is constant.

These results indicate appreciable hydrolysis of lead ion in aqueous solution, and hence, the concentration of lead ion cannot be taken as equal to total lead in the solution at all p_H from zero to seven. The variation in the value of the formation constant of nitrato-lead complex, observed by various workers, might be due to hydrolysis of lead ion in aqueous solution. To verify this, the solubilities of lead iodate in (*i*) sodium perchlorate, (*ii*) perchloric acid, (*iii*) mixtures of sodium perchlorate and perchloric acid, (*iv*) sodium nitrate, (*v*) nitric acid and (*vi*) mixtures of sodium nitrate and nitric acid were determined at 35° by the method described in the previous paper of the authors (*loc. cit.*) and the results are shown in Tables IA, IB, IC, IIA, IIB and IIC respectively.

TABLE IA

$[NaClO_4]$.	$S \times 10^3$.
0.30	9.860
0.25	9 520
0.20	9.175
0.18	9.005
0.16	8.660
0.14	8.485
0.12	8.230
0.10	8 060
0.08	7.720
0.06	7.205
0.04	6.860
0.02	6.515

TABLE IIA

$[NaNO_3]$.	$S \times 10^3$.	$[PbOH^+] \times 10^6$.	$[Complex] \times 10^6$.	K_1.
0.30	13.35	5.379	7.971	4.94
0.25	12.08	5.913	7.163	4.85
0.20	11.55	5.792	5.758	4 97
0.18	11.21	5.808	5.402	5.17
0.16	10.69	5.682	5.008	5 51
0.14	10.27	5.798	4.427	5.00
0.12	9.840	5.757	4.083	5.91
0.10	9.810	5.439	4.371	8.06
0.08	8.810	5.927	2.883	6.08
0.06	8.210	5.562	2.648	7.93
0.04	7.530	5.693	1.837	8.07
0.02	6.840	5.913	0.927	7.84

TABLE Ib

$[HClO_4]$.	$S \times 10^5$.
0.30	15.17
0.25	13.95
0.20	12.73
0.18	12.02
0.16	11.50
0.14	10.98
0.12	10.37
0.10	9 59
0.08	8.980
0.06	8.865
0.04	7.495
0.02	6.530

TABLE IIb

$[HNO_3]$.	$S \times 10^5$.	$[PbOH^+] \times 10^5$.	$[Pb^{2+}] \times 10^5$.	[Complex] $\times 10^5$.	k_1.	K_1.	K.
0.30	20.21	2.520	6.685	10.13	0.113	13.6	5.05
0.25	17.88	2.698	5.793	9.389	0.116	13.9	6.48
0.20	15.79	3.099	5.171	7.520	0 120	12.1	7.27
0.18	14.72	3.368	5 023	6.329	0.121	10.5	7.00
0.16	13.86	3.380	4.545	5.935	0 120	11 0	8.16
0.14	13.00	3.616	4.225	5.159	0.120	10.2	8.72
0 12	11.98	3.886	3.943	4.151	0.118	8.90	8.77
0.10	10.96	4.358	2.982	3.620	0.143	8.31	12.10
0 08	10.180	4.440	2.548	3.192	0.139	8.99	15.70
0.06	9.565	4.087	2.312	3.166	0.106	12.90	22.80
0.04	8 040	4.980	2 096	1.946	0.096	9.86	23.20
0,02	6.845	5.905		0.940		7.96	

DISCUSSION

The solubility of lead iodate in nitric acid is greater than that in sodium nitrate of the same concentration, as observed in the perchloric acid and sodium perchlorate system. The solubilities in nitric acid and sodium nitrate, however, are respectively greater than that in perchloric acid and sodium perchlorate solutions of the same concentration. If the variations in the solubility in sodium perchlorate solutions of different concentrations are assumed to be due to the variation in the ionic strength, the increase in the solubility in sodium nitrate solution of the same ionic strength is most probably due to the formation of nitrato-lead complex. The same argument is applicable to the solutions in nitric acid.

Reactions in Neutral Medium

S_0, S, S_1 and S_2 are respectively the solubilities of lead iodate in sodium perchlorate, perchloric acid (or mixture of sodium perchlorate and perchloric acid), sodium nitrate and nitric acid (or mixture of sodium nitrate and nitric acid) solutions of the same ionic strength.

It has been shown in the previous paper (*loc. cit.*) that in a saturated solution of lead iodate in sodium perchlorate solution, the concentration of lead ion is very small compared to the concentration of $PbOH^+$, and can be neglected. The concentration of $PbOH^+$ is given by equation (7) and can be determined by substituting the values of S_0 and $[IO_4^-]$. In sodium nitrate solution, besides $PbOH^+$, the nitrato complex exists but the ionic strength being the same, the equation (7) holds good. The concentration of iodate ion is $2S_1$. Hence,

$$[PbOH^+] = \frac{S_0^3}{S_1^2} \quad \ldots \quad \ldots \quad (8)$$

TABLE Ic

Mixture		
$[HClO_4]$.	$[NaClO_4]$.	$S \times 10^5$.
0.30	0.00	15.17
0.25	0.05	14.23
0.20	0.10	13.43
0.18	0.12	12.90
0.16	0.14	12.64
0.14	0.16	12.21
0.12	0.18	11.86
0.10	0.20	11.51
0.08	0.22	11.16
0.06	0.24	10.72
0.04	0.26	10.37
0.02	0.28	9.86

TABLE IIc

Mixture								
$[HNO_3]$.	$[NaNO_3]$.	$S \times 10^5$.	$[PbOH^+] \times 10^5$.	$[Pb^{++}] \times 10^5$.	$[Complex] \times 10^5$.	k_1.	K_1.	K.
0.30	0.00	20.21	2.520	6.685	10.33	0.114	13.7	5.05
0.25	0.05	18.99	2.655	5.434	10.89	0.122	13.8	6.68
0.20	0.10	17.79	3.029	4.603	10.16	0.132	11.2	7.36
0.18	0.12	17.11	3.274	4.057	10.78	0.147	11.0	8.76
0.16	0.14	16.60	3.439	3.861	9.260	0.144	8.87	7.99
0.14	0.16	15.92	3.782	3.397	8.741	0.152	7.70	8.58
0.12	0.18	15.48	4.026	2.979	8.425	0.161	6.98	9.43
0.10	0.20	14.80	4.376	2.584	7.840	0.169	5.97	10.10
0.08	0.22	14.38	4.635	2.084	7.661	0.178	5.51	12.30
0.06	0.24	13.69	5.041	1.436	7.313	0.210	4.84	17.00
0.04	0.26	13.44	5.196	0.847	7.447	0.246	4.79	29.30
0.02	0.28	13.35	5.378					

TABLE IIIA

$*\mu$.	$[PbOH.NO_3] \times 10^5$.	$[PbNO_3^+] \times 10^5$.	K.	K_2.
0.30	3.735	6.575	3.28	0.170
0.25	3.271	6.118	4.13	0.134
0.20	3.080	4.440	4.29	0.139
0.18	3.137	3.192	3.53	0.177
0.16	2.980	2.955	4.06	0.161
0.14	2.888	2.271	3.84	0.178
0.12	2.756	1.395	2.95	0.237
0.10	2.651	0.969	3.25	0.274
0.08	2.160	1.032	5.06	0.267

TABLE IIIB

$*\mu$.	$[PbOH.NO_3] \times 10^5$.	$[PbNO_3^+] \times 10^5$.	K.	K_1.
0.30	3.735	6.575	3.28	0.170
0.30	3.821	7.069	4.34	0.135
0.30	4.342	5.818	4.20	0.149
0.30	4.692	6.088	5.00	0.139
0.30	4.929	4.331	3.74	0.229
0.30	5.421	3.320	3.26	0.229
0.30	5.771	2.655	2.97	0.261

μ = Ionic strength.

The concentration of $PbOH^+$ is determined by equation (8) for the sodium nitrate system. The concentraiion of the complex is given by

$$[\text{Complex}] = S_1 - [PbOH^+] \quad \ldots \quad \ldots \quad (9)$$

The simplest reaction for the formation of the complex might be

$$PbOH^+ + NO_3^- \rightleftharpoons PbOH.NO_3 \quad \ldots \quad \ldots \quad (10)$$

without involving any change in the concentration of hydrogen ion. The equilibrium constant K_1 is given by

$$\frac{[PbOH.NO_3^-]}{[PbOH^+] \times [NO_3^-]} = K_1 \quad \ldots \quad \ldots \quad (11)$$

Assuming the whole of the complex to be present as $PbOH.NO_3$, the equilibrium constant is calculated. The concentration of nitrate ion is taken as equal to the concentration of the sodium nitrate since the concentration of the complex is very small compared to the concentration of sodium nitrate. The calculated values of K_1 are shown in Table IIA. The values are fairly constant. Though irregular, there is a tendency of the constant to increase with decreasing ionic strength of the solution. The value of K_1, however, does not strictly indicate the complex to be $PbOH.NO_3$ though it is probable. If the reaction be

$$PbOH^+ + NO_3^- \rightleftharpoons PbNO_3^+ + OH^-,$$

the equilibrium constant would be very nearly constant since the difference in p_H of the various solutions would not be measurable, and the p_H would be very nearly constant. This would, however, be indicated from the solubilities in nitric acid.

Reactions in Acid Medium

In nitric acid Pb^{2+}, $PbOH^+$ and the complex (or complexes) would be in equilibrium with solid lead iodate. The concentration of iodate ion is $2S_2$. Hence,

$$[PbOH^+] = \frac{S_0^3}{S_2^2} \quad \ldots \quad \ldots \quad (12)$$

In perchloric acid (of the same concentration as nitric acid), the solubility is S. According to equation (3), $4S^3$ is equal to $(K_s \times [H^+] + K_s k_1)$. $K_s \times k_1$ is equal to $4S_0^3$. Hence,

$$4S^3 = 4S_0^3 + K_s \times [H^+] \quad \ldots \quad \ldots \quad (13)$$

Substituting the value of K_s from equation (2), the equation (13) reduces to

$$4S^3 - 4S_0^3 = [Pb^{2+}] \times [IO_3^-]^2 \quad \ldots \quad \ldots \quad (14)$$

S and S_0 are the solubilities in sodium perchlorate and perchloric acid, and the former is constant if ionic strength is constant, and the latter is constant if p_H and ionic strength are constant. Hence, the product of the concentration of lead ion and square of the concentration of iodate ion is constant at a given p_H and ionic strength and is equal to $(4S^3 - 4S_0^3)$. In nitric acid (or mixture of nitric acid and sodium nitrate) of the same p_H and the same ionic strength as perchloric acid (or mixture of perchloric acid and sodium perchlorate), the equation (14) would hold good. The concentration of lead ion is given by

$$[Pb^{2+}] = \frac{S^3 - S_0^3}{S_2^2} \quad \ldots \quad \ldots \quad (15)$$

The concentration of the complex (or complexes) is

$$[\text{Complex}] = S_2 - [Pb^{2+}] - [PbOH^+] \quad \ldots \quad (16)$$

The complex might be PbOH. NO_3 or $PbNO_3^+$ or both. The formation of the latter may be represented by equation (17) and equilibrium constant K by (18).

$$Pb^{2+} + NO_3^- \rightleftharpoons PbNO_3^+ \quad \ldots \quad \ldots \quad (17)$$

$$\frac{[PbNO_3^+]}{[Pb^{2+}] \times [NO_3^-]} = K \quad \ldots \quad \ldots \quad (18)$$

Assuming the whole of the complex to be either $PbOH.NO_3$ or $PbNO_3^+$, the constants K_1 and K are calculated. The values are shown in Table IIB and IIc. Neither K nor K_1 are strictly constant. The former increases and the latter decreases with decreasing concentration of hydrogen ion. Besides, K is very nearly constant at the higher hydrogen ion concentration and changes rapidly towards lower acid concentration range. The variation of K_1 is just opposite to that of K, and is very nearly constant values are found at the lower acid concentration range. The value of K_1 in lower acid range in Table IIc is very nearly 5 and agrees with the value obtained in the neutral solution (Table IIA) at about ionic strength of 0.3. The value of K_1 in pure nitric acid series (Table IIB) in the lower acid range (ionic strength, 0.02) is very nearly the same as that obtained in the neutral solution at about the same ionic strength.

These results indicate the existence of both the complexes $PbNO_3^+$ and $PbOH.NO_3$ in nitric acid or mixture of nitric acid and sodium nitrate solution. The complex in neutral solution is most probably $PbOH.NO_3$.

Using the values of K_1, obtained with sodium nitrate solution at a particular ionic strength, and the value of $[PbOH^+]$ and $[NO_3^-]$ in nitric acid or mixture of sodium nitrate and nitric acid of the same ionic strength, the values of $[PbOH.NO_3]$ were calculated. The concentration of $PbNO_3^+$ was obtained by subtracting $[PbOH.NO_3]$ from [complex]. The values of K_1 were recalculated, and shown in Tables IIIA and IIIB respectively for pure nitric acid and mixture of sodium nitrate and nitric acid series. The results, though not very good, may be taken as constant. The equilibrium constants of the reaction

$$PbNO_3^+ + H_2O \rightleftharpoons PbOH.NO_3 + H^+ \quad \ldots \quad (19)$$

given by equation (20) is also calcutated.

$$\frac{[PbOH.NO_3] \times [H^+]}{[Pb\ NO_3^+]} = K_2 \quad \ldots \quad \ldots \quad (20)$$

The calculated values are shown in Tables IIIA and IIIB. The hydrolysis constant k_1 is also calculated by equation (5). The mean values of K, K_1, K_2 and k_1 at ionic strength 0.3 are 3.83, 4.94, 0.186 and 0.161 respectively. It is interesting to note that K and K_1 are very nearly equal, and K_2 and k_1 are also very nearly equal. The value of k_1 obtained agrees with those reported in the previous paper by the authors.

DEPARTMENT OF CHEMISTRY,
RAVENSHAW COLLEGE,
CUTTACK-3.

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ELECTRODEPOSITION OF CHROMIUM-MOLYBDENUM ALLOYS

By S. C. Shome

Alloys of chromium and molybdenum, containing small amounts of the latter metal, have been deposited from solutions prepared by dissolving molybdic acid to the standard chromium plating solution. Bright, semi-bright and dull deposits of the alloys are obtained; the dull metallic plates become bright after polishing. The optimum conditions for the deposition of the alloy have been determined. An alloy containing 1·7% of molybdenum is deposited from a bath containing 400 g./litre CrO_3, 360 g./litre H_2MoO_4 and 4 g./litre H_2SO_4 at 40° and a current density of 1 amp./sq. in. The deposits formed at higher current densities contain higher percentages of molybdenum and some oxygen.

Industrial chromium plating (Fink, U. S. P. 1,581,188/1926) has been widely used for decorative and protective finishing of metals. Several publications have dealt with the chromium plating but there is very little of information on the subject of electrodeposition of chromium alloys. Fuseya and Sasaki (*Trans. Electrochem. Soc.*, 1931, **59**, 445) reported that a chromium-iron alloy containing more than 16% chromium was deposited electrolytically from the sulphate bath using copper cathodes and magnetite anodes. The chromium plating bath, with iron salts added, did not furnish any good deposit of the alloy. Skalozubov and Vlasova (*Zvest. Novocherkasskogo Ind. Inst. Im. S. Ordzhonikidze*, 1940, **6**, 15; cf. *Chem. Abst.*, 1941, **35**, 1323) found that the electrodeposition of a protective chromium-nickel coating was possible from a solution containing chromic acid, nickel sulphate and boric acid. Skalozubov and Goncharova (*ibid.*, 1940, **6**, 24) described the electrodeposition of iron-chromium-nickel alloys from a solution containing chromic acid, nickel sulphate, ferrous sulphate and boric acid. A corrosion-resistant alloy containing tungsten, chromium and nickel was electrodeposited by Fuchs (B. P. 397,789/1933). Rogers and Burr (*J. Electrochem. Soc.*, 1950, **97**, 67) obtained electrodeposited chromium-tungsten alloys from a solution of chromic acid, reduced to the trivalent chromium with ammonium citrate, and containing tungstic anhydride.

A good deposit of molybdenum has not been obtained by the electrolysis of its aqueous solution, because molybdenum is one of the metals which are self-polarising (Price and Brown, *Trans. Electrochem. Soc.*, 1936, **70**, 423). When, however, any of the metals such as cobalt, nickel, iron, copper and tungsten was present, molybdenum was easily deposited in the form of an alloy (Myers, 1941, Dissertation for the degree of Doctor of Philosophy, Columbia University, N. Y. C.; Elwee and Holt, *J. Electrochem. Soc.*, 1952, **99**, 48; Yntemma, U. S. P. 2,428,404/1947). Considering the possibility of chromium, acting as a carrier of molybdenum in the process of electrodeposition, the present work was undertaken.

Experimental

Plating Solution.—The solution was prepared by adding a weighed amount of molybdic acid to the chromium plating bath containing 400 g./litre of chromic anhydride. The molybdic acid was dissolved in the chromic acid solution containing the necessary amount of sulphuric acid by efficient stirring with a glass rod.

Electrolysis.—The solution was heated to the required temperature and electrolysed in a 250 c.c. pyrex beaker. Pure copper sheet was used as the cathode and a lead-tin alloy containing 10% tin was used as the anode. The copper specimen, before serving as the cathode, was polished, washed with soap water and then degreased in the vapour of trichloroethylene. The specimen was weighed before and after electrolysis so as to determine the weight of the deposit formed on the cathode. The electrolysis of the solutions was carried out under varied conditions, employing a fresh solution for each experiment.

Analysis of Deposit.—The deposit obtained on the cathode was dissolved in warm 2*N*-HCl and to this solution was added a mixture of 9 c.c. HCl (conc.) and 1 c.c. of HNO_3 (conc.). HNO_3 was added to oxidise the molybdenum to hexavalent state and HCl was used to prevent any slight oxidation of chromium (the trivalent chromium was not oxidised in the presence of sufficient HCl). The solution of chromium and molybdenum was then evaporated almost to dryness in a porcelain basin over a water-bath. The removal of the acid was necessary as otherwise when the solution was treated subsequently with ammonia to precipitate chromium, ammonium salts were formed and chromium salts became easily soluble in excess of ammonia in the presence of ammonium salts. The solution containing chromium and molybdenum salts was then diluted with distilled water and made up to volume in a 50 c.c. volumetric flask. A portion of this stock solution was then treated with a slight excess of ammonia, when chromium was precipitated as hydroxide and molybdenum remained in the solution as molybdate.

The solution was then heated to boiling, filtered and the precipitate was washed thoroughly with hot water. The filtrate and the wash-water were kept aside for molybdenum estimation. The gelatinous chromium hydroxide precipitate, which had absorbed some molybdenum, was again dissolved in warm dilute HCl and the precipitation with ammonium hydroxide was repeated. The two ammoniacal filtrates were then combined and evaporated to a small volume. The molybdenum in the solution was determined by the colorimetric titration method using ammonium thiocyanate and stannous chloride solutions (Grimaldi and Wells, *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 315). To run a blank, a pure chromium deposit was treated similarly and the experiment showed the absence of molybdenum in the deposit.

The chromium hydroxide precipitate was dissolved in HCl (dil.), made alkaline with NaOH and oxidised to chromate by adding H_2O_2 solution. The chromate solution was then heated to boiling to decompose the excess H_2O_2, cooled, acidified with HCl and titrated iodimetrically.

The results of the experiments carried out under various conditions are recorded in Tables I to IV.

TABLE I

Effect of concentration of molybdic acid.

CrO_3 in soln. = 40 g./100 c.c. C.D. at cathode = 1 amp./sq. in. Temp. of soln. = 40°.
SO_4/CrO_3 in soln. = 1/100.

H_2MoO_4 taken (g/100 c.c.)	Voltage of cell.	Time of electrolysis.	Wt. of deposit.	% Current efficieney.	Mo in the deposit.	Cr in the deposit.	Appearance of the deposit.
0	3.1	15 min.	0.0224 g.	13 9	Nil	99.2%	Bright, metallic
2	,,	,,	0.0220	13.6	,,	...	,, ,,
6	3.2	,,	0.0190	11.7	,,	...	,, ,,
12	,,	30	0.0308	9.5	Traces	...	,, ,,
24	3 4	,,	0 0128	4.0	0.60%	97.9	,, ,,
30	3.7	45	0.0304	6.3	1.2	97.6	Semi-bright
36	4 0	,,	0.0264	5.4	1.7	98.1	Dull, metallic

TABLE II

Effect of temperature.

CrO_3 in soln. = 40 g./100 c.c. C.D. at cathode = 1 amp./sq. in.
SO_4/CrO_3 in soln. = 1/100.

Temp. of soln.	H_2MoO_4 taken.	Voltage of cell.	Time of electrolysis.	Wt of deposit.	% C.E.	Mo in the deposit.	Cr in the deposit.	Appearance of the deposit.
40°	0 g.	3.1	15 min.	0.0224 g.	13.9	...	...	Bright, metallic
,,	36	4.0	45	0.0264	5.4	1 7%	98.1%	Dull, ,,
25°	0	3.3	15	0.0437	27.0	...	...	,, ,,
,,	36	4.4	45	0.0426	8.8	1.1	96.2	,, ,,
10°	0	3.5	15	0.0600	37.1	...	...	Burnt
,,	36	4.8	45	0.0477	9.8	1.7	96.4	Grey

TABLE III

Effect of current density.

CrO_3 in soln. = 40 g./100 c.c. Temp. of soln. = 40°. SO_4/CrO_3 in soln. = 1/100.

C.D. at cathode. (amp/sq.in)	H_2MoO_4 taken*	Voltage of cell.	Time of electrolysis.	Wt of deposit.	% C.E.	Mo in the deposit.	Cr in the deposit.	Appearance of the deposit.
0.5	0	2.9	30 min.	0.0150 g.	.3	...	...	Bright, metallic
,,	36	3.4	90	0.0156	3.2	1.2%	98.0%	,, ,,
1	0	3.1	15	0.0224	13.9	...	...	,, ,,
,,	36	4.0	45	0 0264	5.4	1.7	98.1	Dull, ,,
2	0	3.4	15	0.0319	19.7	...	...	Bright, ,,
,,	36	4.5	45	0.0237	4.9	2.1	93.6	Dull, ,,
4	0	3.8	15	0 0840	26.0	...	...	Burnt
,,	36	6.4	30	0.0100	1.5	5.8	85.6	Grey

* (g/100 c.c.)

TABLE IV

Effect of concentration of H_2SO_4.

CrO_3 in soln. = 40 g./100 c.c. C.D. at cathode = 1 amp./sq. in. Temp. of soln. = 40°.

SO_4/CrO_3 in soln.	H_2MoO_4 taken.	Voltage of cell.	Time of electrolysis.	Wt. of deposit.	% C.E.	Mo in the deposit.	Cr in the deposit.	Appearance of the deposit.
1/200	0 g.	3.1	15 min.	0.0045 g.	2.8	...	...	Bright, metallic
,,	36	4.0	45	...	...	...	...	Brown-black oxide (Cr & Mo present)
1/100	0	3.1	15	0.0224	13 9	...	...	Bright, metallic
,,	36	4.0	45	0 0264	5.4	1.7 %	98.1 %	Dull, metallic
1/50	0	3.4	15	0.0165	10.2	...	...	Bright, ,,
,,	36	4 0	45	0.0145	3.0	0 8	97.1	,, ,,
1/25	0	2.4	15	No deposit	...	...	...	... ...
,,	36	3.8	45	Slight	...	...	...	Bright, metallic

DISCUSSION

As the concentration of molybdic acid in the solution is increased, the deposits obtained at the cathode contain higher percentages of the molybdenum metal (Table I). However, the amount of molybdic acid in the chromic acid solution could not be increased to more that 36 g./100 c.c. of the plating solution ; the reddish yellow molybdenum chromate was precipitated from the solution with more than this quantity of molybdic acid. The appearance of the electrodeposit changes from bright to dull with the increasing amount of molybdenum in the coating. The dull appearance appears to be due to the fine structure of the deposited crystal and the deposits show metallic lustre when polished. The voltage of the bath is higher with the increase of molybdic acid content of the solution. This might be due to the higher viscosity of the electrolyte or due to the formation of stable compounds of chromium and molybdenum in the solution. The low current efficiency of the alloy deposition seems to be due to the small amount of molybdenum in the deposit, favouring evolution of hydrogen.

The molybdenum content of the electrodeposit did not vary much with the change of the temperature of the plating bath, though a slightly lower value was obtained at 25° (Table II). The appearance of the coatings becomes inferior with the decrease of the temperature of the solution. The current efficiency of the cathodic process increases with the decrease of temperature and this is true whether the electrolyte contains any molybdic acid or not. Electrodeposition at a temperature higher than 40° could not be carried out, since the reddish yellow molybdenum chromate was precipitated as the temperature was raised.

The molybdenum content of the deposits was higher with the increase of the C. D. at the cathode and at C. D. higher than 1 amp./sq. in. The deposit contained a certain percentage of oxide (Table III). A bright alloy of chromium and molybdenum containing 1.2% of molybdenum is formed at a C. D. of 0.5 amp./sq. in., but

in this case both the current efficiency and the throwing power are so low that the cathode surface is not completely covered with the alloy coating even after 90 minutes of electrolysis.

The chromium-molybdenum alloy is best obtained when the SO_4/CrO_3 ratio in the plating solution is 1/100, which is also the optimum value for chromium plating (Table IV). At the lower concentration of sulphuric acid, an oxide coating containing both chromium and molybdenum is formed. A bright coating containing 0.8% of molybdenum was produced when the SO_4/CrO_3 ratio was 1/50, but in this case the cathode was only partly coated owing to the poor throwing power of the solution.

The author is much indebted to Professor C. G. Fink, Head of the Division of Electrochemistry, Columbia University, U.S.A., since deceased, for suggesting the problem. The experimental part of the investigation was carried out in the Electrochemical Laboratory of the Columbia University.

Department of Chemistry,
Presidency College, Calcutta.

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ELECTROLYTIC ZINC POWDER

By S. C. Shome

Spongy zinc has been prepared by the electrolysis of sodium zincate solution at room temperature; the sponge crumbles to a fine powder when washed with water and dried. Brass is found to be the suitable cathode and zinc, the anode. Zinc sponge is best obtained from a solution containing 20 to 30% NaOH and 3 to 6% zinc at a cathodic C.D. of 20 to 35 amp./dm^2. The average current efficiency of zinc deposition is 78%.

In obtaining one pound of zinc powder by the electrolysis of sodium zincate solution using a rotating zinc anode, half immersed in the electrolyte, 0.7 Kw/hr. of electrical energy is required. If an insoluble anode, such as nickel, is employed, 1.5 Kw/hr. of energy is consumed per pound of zinc powder produced.

Zinc powder finds extensive use as a reducing agent in various chemical processes. It is an essential material for the manufacture of sodium hydrosulphite and Rongalite C, which are largely employed in the reduction of dyestuffs in textile industries. Zinc powder is also required for the production of zinc alloys in powder metallurgy.

The methods which can be employed for the preparation of zinc powder are as follows: (*i*) as a byproduct in the pyrometallurgy of zinc, (*ii*) by the application of a jet of air to atomize a column of molten zinc, and (*iii*) by the electrolysis of zinc salt solutions. The powder obtained by method (*iii*) is chemically more active than that obtained by any of the other methods.

Morgan and Ralston (*Chem. Met. Eng.*, 1916, **15**, 465) studied the formation of zinc sponge from zinc sulphate, zinc chloride or sodium zincate solution by the electrolytic method; the sponge obtained by electrodeposition crumbled to a fine powder when dried. Sebborn (*Trans. Faraday Soc.*, 1933, **29**, 825) studied the formation of zinc sponge by the electrolysis of zinc sulphate solution and was of the opinion that the formation of zinc sponge was linked up with the production of zinc hydroxide at the cathode. He found that the spongy deposit of zinc from sulphate solution was favoured by low concentration of metal ion and by the use of high current densities. Sebborn (*ibid.*, 1933, **29**, 659) further showed that the zinc powder was spontaneously oxidised to zinc oxide with evolution of heat, when the powder was coated with a thin film of alkali and exposed to air. He considered that sodium and potassium hydroxides dissolved the surface film of the oxide from the metallic zinc, forming sodium zincate and potassium zincate respectively. The combined effect of the heat of this reaction and the removal of the protective oxide film from the zinc powder caused further oxidation of the zinc powder.

Morgan and Ralston (*loc. cit.*) electrolysed sodium zincate solution at 4.5 volts, employing a stationary zinc anode and an iron cathode. In the present investigation zinc has been deposited from sodium zincate solution at 1.4 volts using a slowly rotating zinc anode. This device saves more than 50% of electrical energy consumed per pound of zinc powder. At this low voltage oxygen does not evolve at the anode during electrolysis and, hence, the concentration of zinc ion in the solution remains unchanged. Further, it is observed that brass is a better cathode material than iron, since the hydrogen overvoltage on brass has a higher value than on iron. The other optimum conditions for the production of zinc powder by the electrolysis of sodium zincate solution have also been studied.

Experimental

The sodium zincate solution was prepared by dissolving freshly precipitated zinc hydroxide in sodium hydroxide solution and was electrolysed in a glass beaker at room temperature. The average current efficiency of zinc deposition was 78%. The electrolytic zinc powder contained 93 to 94% zinc.

The various conditions under which spongy zinc has been deposited from zincate solution are summarised in Table I. The electrolysis of sodium zincate solution, employing an insoluble anode, produced oxygen at the anode and the concentration of zinc ion in the solution gradually decreased (Expt. 1, Table I). Similar evolution of oxygen was observed at high current densities even when zinc was the anode material. There was, however, no oxygen evolution during the electrolysis of zincate solution when the C. D. at the zinc anode was low. But after one hour, the voltage of the cell gradually increased from 1.2 to 4.0 and oxygen evolution commenced at the anode (Expt. 3). The rise in voltage and the oxygen evolution at the zinc anode could be prevented by any of the following methods: (*a*) decreasing the anode current density, (*b*) slowly stirring the liquid near the anode surface, (*c*) slowly rotating the anode when it was circular, and

(*d*) removing the black film from the anode surface from time to time. The circular zinc anode was half immersed in the electrolyte and was slowly rotated to and fro manually during electrolysis. The use of Ni as an insoluble anode resulted in the decrease of zinc ion concentration in the solution. The attempt to replenish zinc slowly by keeping an asbestos bag containing zinc hydroxide in suspension in the anolyte was not satisfactory.

Zinc was also deposited in spongy form by the electrolysis of zinc sulphate solution (2 to 3% $ZnSO_4$, $7H_2O$) using zinc anode and aluminium cathode. This method was found unsuitable for practical purpose, since the electrical resistance of dilute zinc sulphate solution was high and the current efficiency of zinc deposition from such a solution was low.

TABLE I

Electrodeposition of zinc from zincate solution.

Temperature of solution = 25° to 28°.

Expt. No.	Conc. of NaOH (g./100 c.c.)	Zn content of soln. (g./100 c.c.)	Cathode.	Anode.	C.D. (amp./dm²) at Cathode.	C.D. (amp./dm²) at Anode.	Voltage of cell.	Remarks.
1	20	4.0	Brass	Nickel	35	16	3.2	Oxygen evolved at anode and Zn^{2+} conc. in soln. gradually decreased.
2	30	6.6	,,	Zinc (stationary)	30	16	4.5	Same as in Expt. 1.
3	20	4.0	,,	,,	20	6	1.2	No oxygen evolution at anode and Zn^{2+} conc. in soln. did not change for one hour.
4	20	4.0	,,	Zinc disc* (rotating)	20	16	1.4	No oxygen evolution at anode and Zn^{2+} conc. in soln. remained unaltered.
5	20	3.5	,,	Nickel [enclosed in asbestos bag containing $Zn(OH)_2$ suspended in zincate soln.].	20	16	4.5	Oxygen evolved at anode. Half the zinc deposited came from $Zn(OH)_2$ dissolved in anode chamber.

* Half immersed in the electrolyte.

The electrolytic zinc powder, when washed thoroughly with water to make it free from alkali, could be dried without any difficulty. For determining zinc content, the sodium zincate solution was acidified with 6*N*-H_2SO_4 and titrated with $K_4Fe(CN)_6$ using diphenylamine as internal indicator. The purity of the zinc powder was estimated by the ferric alum method as developed by Edwards (*Chem. Met. Eng.*, 1919, **21**, 192).

DISCUSSION

Reactions at the Cathode.—During the electrolysis of sodium zincate solution, the reactions occurring at the cathode are:

$$Zn(OH)_4^{2-} + 2e^- = Zn + 4OH^- \quad \ldots \quad (1)$$

and

$$2H^+ + 2e^- = H_2 \quad \ldots \quad (2)$$

The formation of hydrogen molecules by the discharge of hydrogen ions is a highly polarised reaction (eq. 2), and even at high current densities mostly zinc is deposited on the cathode (eq. 1). The hydrogen overvoltage on brass has a higher value than the same on iron; brass is therefore found to be a better cathode material than iron for electrodeposition of zinc.

Zinc is deposited in powdery form as the zincate solution is electrolysed. At the commencement of electrodeposition zinc nuclei are formed at the cathode surface and then grow to small particles as the electrolysis continues. The sodium zincate solution also contains colloidal particles of zinc hydroxide, which are negatively charged. At high current densities zinc hydroxide is deposited in a thin layer around the growing zinc particles and puts a stop to their further growth. This happens when the concentration of colloidal zinc hydroxide at the cathode surface increases in proportion to zinc ion concentration. New zinc nuclei are then formed and the process is repeated. Zinc is thus obtained at the cathode in the form of fine powder coated with a thin layer of hydroxide.

Reactions at the Anode.—The anodic reactions are:

$$Zn + 4OH^- = Zn(OH)_4^{2-} + 2e^- \quad \ldots \quad \ldots \quad (3)$$

and

$$2OH^- = \tfrac{1}{2} O_2 + H_2O + 2e^- \quad \ldots \quad \ldots \quad (4)$$

When an insoluble anode, such as nickel, is used (Expt. 1), oxygen is evolved by the discharge of OH^- ions (eq. 4). With a zinc anode, the soluble zincate ions are formed (eq. 3) and the anodic product removes itself continuously from the anode surface. At a sufficiently high C.D., the liquid next to the anode surface becomes saturated with sodium zincate, and then other anodic processes, such as discharge of OH^- ions requiring a higher electric energy consumption, become possible. As OH^- ions are discharged, first of all an oxide film is formed, followed by the evolution of oxygen. The presence of an oxide film on the zinc surface will hinder further production of zincate ions by the dissolution of the zinc anode. This anodic passivity may be avoided if the liquid near the anode surface is slowly stirred so that fresh alkali can attack the zinc surface. This stirring can be conveniently effected by employing a slowly rotating circular anode, half immersed in the electrolyte (Expt. 4).

With a stationary anode, the insoluble film formed on its surface at high current densities is loose and can easily be removed by scratching with a glass rod. Once this film is removed, the anodic polarisation is reduced and electrolysis proceeds again at a low voltage without any evolution of oxygen. This is in accord with Evans' theory ("Metallic Corrosion, Passivity and Protection", Arnold, 1946, p. 15) which attributes passivity of metals to the formation of insoluble films on their surfaces.

The author wishes to express his sincere thanks to Dr. J. C. Ghosh for his interest in the work and encouragement. The experimental part of this investigation was carried out at the Chemical Laboratories of the Indian Institute of Science, Bangalore.

Chemical Laboratory,
Presidency College, Calcutta.

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ON THE ANALYTICAL APPLICATIONS OF DUTOIT'S THERMO-VOLUMETRY: ESTIMATION OF AMINO-ACIDS

By Kumar Krishna Chatterjee and Ajit Kumar Ghosh

The thermometric method has been employed in the estimation of some biologically important amino-acids, both individually and in mixtures, by titration with NaOH. The method is rapid and non-specific and the results obtained agree within 2% of the theoretical values.

The usefulness of thermometric titration in ascertaining the stages of ionisation of the polybasic acids was first shown by Dutoit (*J. chim. phys.*, 1922, **19**, 324, 331), who titrated H_2SO_4 and H_3PO_4 with NaOH and obtained in the thermometric diagrams, inflexions indicating the stagewise replacement of H^+ by Na^+. Later, Mondain-Monval and Paris (*Bull. soc. chim.*, 1938, *v*, **5**, 1641) titrated a number of other acids including H_3AsO_3, H_3AsO_4 and H_3BO_3 with NaOH, obtaining definite evidence of the formations of NaH_2AsO_3, NaH_2AsO_4, Na_2HAsO_4, Na_3AsO_4 and NaH_2BO_3 in solution. Recently Paris and Robert (*ibid.*, 1943, **10**, 224) and Tardy and Paris (*ibid.*, 1945, **12**, 16) have applied thermometric method in the estimation of mixtures of oxy-acids of phosphorus by a single titration with NaOH.

The determination of the basicity of a polybasic acid by the thermometric method is obviously due to the large differences in the heats of ionisation corresponding to the successive stages of the dissociation of the acid molecule. The same reason also accounts for the applicability of the method in the estimation of the acid mixtures. The above considerations have led the authors to test the applicability of thermometric titration in the estimation of some biologically important amino-acids, in view of the fact that except the formol titration method of Sörensen, other methods, which are based on changing the physical surroundings of the ampholytes, are of limited applicability, and hence, they are of little value from the analytical standpoint.

Attempt has been made to titrate both $-COOH$ and $-NH_2$ with NaOH and HCl respectively. Though considerable success has been attained in the estimation of the acid group, both for the individual acid as well as of their mixtures, the method failed in the titration of the basic part due to the smallness of the heat change.

Experimental

Stock solutions of glycine (0.23 *N*), alanine (0.1134 *N*), glutamic acid (0.08965 *N*) and aspartic acid (0.0725 *N*) were prepared by dissolving in distilled water accurately weighed samples of Merck's A.R. amino-acids, which were purified by recrystallising twice from distilled water and drying at 100° in the air-oven.

These solutions were employed for the titration of the individual amino-acid with a standard NaOH solution. Solutions of the amino-acids at different concentrations were prepared by the requisite dilution of the stock solutions with distilled water.

A second set of stock solutions of glycine (0.1002 *N*), alanine (0.0782 *N*), glutamic acid (0.0863 *N*) and aspartic acid (0.0644 *N*) were prepared by the same method as above.

These solutions were employed in the titrations of the mixtures of the amino-acids at different compositions.

A stock solution of 2*N*-NaOH in freshly distilled water was prepared by dissolving E. Merck's NaOH, and standardising against 0.098 *N*-H_2SO_4, using phenolphthalein indicator. The stock alkali solution was diluted to various strengths with distilled water, the solutions being immediately restandardised before employing them in the thermometric titration of the amino-acid.

The thermometric apparatus and the method of titration were the same as Dutoit's. The individual acids or their mixtures (50-100 c.c.) were employed for titration (*loc. cit.*).

In Tables I-III the results of the thermometric titrations of the amino-acids have been summarised. The titrations are very well reproducible, as has been shown by duplicate experiments.

The thermometric curves (Figs. 1-5) have been drawn by plotting the heat changes at constant volume ΔT_{cv} against the volume of the titre added. Here

$$\Delta T_{cv} = \frac{\Delta T\,(V + dv)}{V},$$

where ΔT = observed change in temperature, V = the initial volume in c. c. of the solution in the Dewar and dv is the volume in c.c. of the titre added). This method of plotting is due to Chatterjee (this *Journal*, 1955, **32**, 366).

The compositions of the acid mixtures have been calculated in the following way:

Dibasic acid. Volume of the titre at first inflexion × strength of the base × M. W. of the dibasic acid = wt. in g. of the dibasic acid per litre.

Monobasic acid. (Volume of the titre at the second inflexion − 2 × volume of the titre at the first inflexion) × M.W. of the monobasic acid = wt. in g. of the monobasic acid per litre.

TABLE I

Thermometric titrations of amino-acids with NaOH.

	Glycine (Fig. 1).		Alanine (Fig. 2).	Glutamic acid (Fig 3).		Aspartic acid (Fig.4)			
End points.	Curve (a).	Curve (b).	Curve (c).	Curve (a).	Curve (b).	Curve (a).	Curve (b).	Curve (a).	Curve (b).
Thermometric (c.c.)	11.4	5.7	11.35	5	6.1	4.5 9	5.3 10.6	4.75 9.55	3.2 6.4
Theoretical (c.c.)	11.42	5.74	11.42	5	6.07	4.45 8.9	5.41 10.82	4.80 9.59	3.125 6.25
% Error in thermometry	+ 0.2	−0.75	− 0.64	Nil	+0.5	+1.12%	− 1.6%	−0.5	+2.7

TABLE II

Thermometric titration of mixtures of amino-acids with NaOH (Fig. 5)

End-points.	Curve (a).	Curve (b).	Curve (c).
Thermometric (c.c.)	4.5 14.4	3.65 11.40	3.4 9.8
Theoretical (c.c.)	4.509 14.25	3.607 11.40	3.37 10.00
% Error :			
First inflexion	−0.2 %	+1.3 %	1.2 %
Total	+1%	Nil	~2%

TABLE III

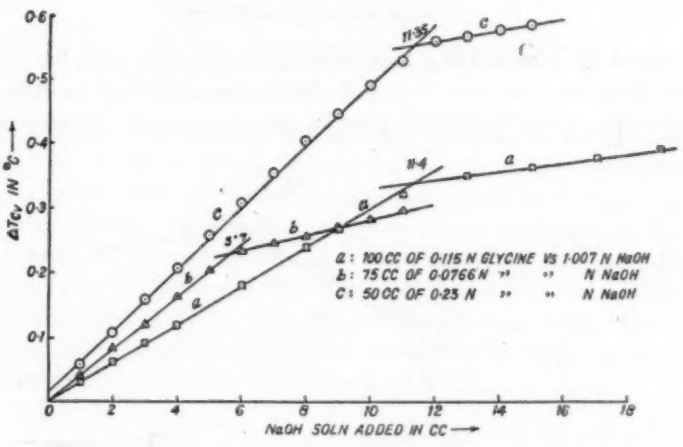
Composition of the mixtures of amino-acids from thermometric titration curves (Fig. 5).

	Glycine		Glutamic acid		Alanine.	Aspartic acid.
	Curve (a)	Curve (b).	Curve (a).	Curve (b).	Curve (c).	Curve (c).
Found (in g.)	0.1915	0.1504	0.3167	0.2569	0.1393	0.2166
Actually present (in g.)	0.1872	0.1498	0.3175	0.2540	0.1393	0.2145
% Error	+ 2.26	+0.4	−0.25	+1.14	+0.014	+0.93

DISCUSSION

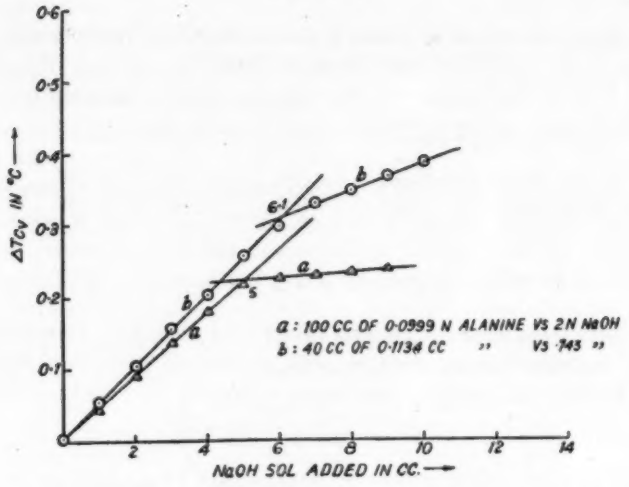
It will be seen from the Figs. 1-5 and Tables I-III that the thermometric titration curves of the individual amino-acids as well as those of mixtures of these acids are all characterised by sharp end-points, which agree within 2% (usually less) of the theoretical

FIG 1



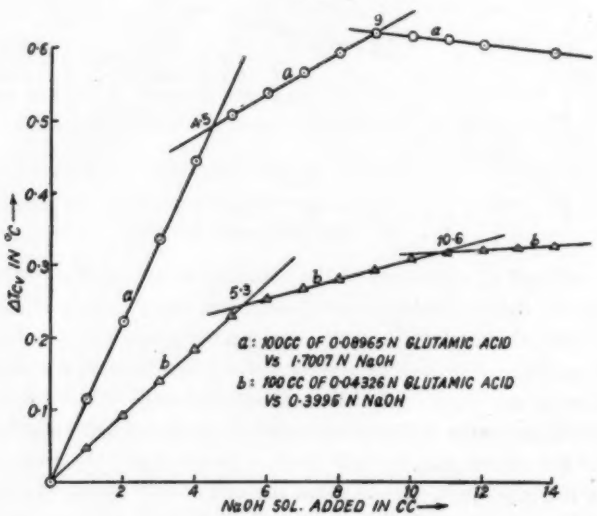
values. As a method of estimation of the potential acidity of these substances in aqueous medium within the range of concentration employed (0.2 N − 0.03 N acids), thermometric titration with NaOH therefore presents considerable promise. The basicity is clearly indicated by the number of inflexions arising in the thermometric diagrams. In the curves of the dicarboxylic acids, viz., glutamic and aspartic acids (Figs. 3 & 4), the difference in the extent of the ionisation of the two carboxyl groups is also reflected in the difference in the slopes of the intersecting straight lines. As expected, the first half of the curve is steeper than the other half, showing that the rate of heat change during the replacement of the first H^+ is greater than that of the second. In fact, the first acid dissociations of glutamic and aspartic acids (pk_1 = 4.2 and pk_1 = 3.8 respectively) are strong enough to be titrated directly by potentiometric method. In the same way differences in the acid strengths of the mono- and the dicarboxylic acids are indicated in their thermometric titration curves.

FIG 2



In the case of the mixtures of a mono-and a dicarboxylic acid, the breaks in the thermometric diagrams are also in accord with the magnitudes of the dissociation constants of these acids. Since the second dissociation constants of glutamic and aspartic

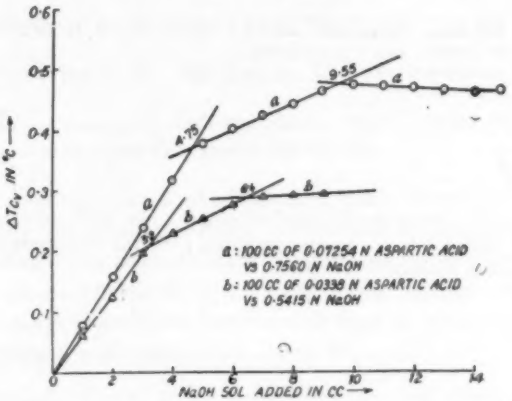
FIG 3



acids ($pk_2 = 9.8$ and $pk_2 = 9.9$ respectively) are very nearly equal to those of glycine and alanine ($pk = 9.7$ in both cases), it follows that the acid salt of the dibasic acid and the monobasic acid should be simultaneously neutralised by NaOH and the end-point of the titration will be due to the total acids present in the system. The two breaks arising in

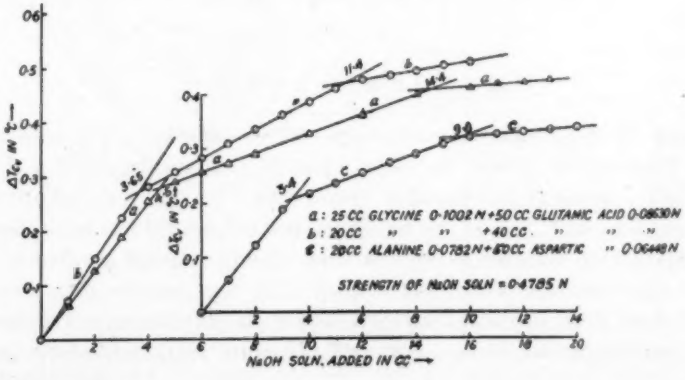
the thermometric titration curves of the mixtures (Fig. 5) occur in their expected positions, the first one indicating the formation of the acid salt of the dicarboxylic acid, the other one giving the total acid content of the mixtures.

FIG 4


ΔTcv IN °C
NaOH SOL. ADDED IN CC
a : 100 CC OF 0·07254 N ASPARTIC ACID Vs 0·7560 N NaOH
b : 100 CC OF 0·0338 N ASPARTIC ACID Vs 0·5415 N NaOH

The explanation of the failure of thermometric titration by HCl in the estimation of the amino group due to the smallness of the heat change, is also provided if we consider the values of the heats of formation of the Zwitterion acid ZH^+ and the Zwitterion base ZOH^- respectively. These values, which have been determined by Owen (*J. Amer. Chem. Soc.*, 1924, **46**, 24) and Sturtevant (*ibid.*, 1941, **63**, 88 ; 1942, **64**, 762) from measurements of the temperature coefficients of the ionisation constants and the heats of reactions of glycine and *dl*-alanine with HCl and NaOH respectively, show that the heat of the formation of the Zwitterion base ZOH^- is considerably larger than the corresponding values for the formation of the Zwitterion acid ZH^+.

FIG 5


ΔTcv IN °C
NaOH SOLN. ADDED IN CC
a : 25 CC GLYCINE 0·1002 N + 50 CC GLUTAMIC ACID 0·0853 N
b : 20 CC " " + 40 CC " " "
c : 20 CC ALANINE 0·0782 N + 60 CC ASPARTIC " 0·0644 N
STRENGTH OF NaOH SOLN = 0·4785 N

The thermometric method of the estimation of the amino-acids so far developed is simple, quick, fairly accurate and non-specific. It thus combines all the features of a generalised method, its only limitation being that it cannot be carried out at very low concentrations due to the difficulty in the accurate determination of extremely small heat changes, with the present equipment.

DEPARTMENT OF PHYSICAL CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY,
CALCUTTA-9

Received December 20, 1956.

N.B. The results of the thermometric titrations of the amino-acids have expediently been interpreted from classical standpoint due to the inadequacy of the Zwitterion concept as applied to the dicarboxylic amino-acids in general.

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SEARCH FOR NEW INSECTICIDES. PART XII

By A. B. Sen and A. K. Sen Gupta

Several phenothiazines containing methoxy, ethoxy, chloro, methyl and ethyl grouping have been synthesised with a view to testing their insecticidal activity.

The insecticidal properties of phenothiazine were discovered during an investigation of the toxicity of organic sulphur compounds to mosquito larvae (Campbell *et al.*, *J. Econ. Entomol.*, 1934, **27**, 1176). Subsequent investigations established the effectiveness of the phenothiazine as a stomach poison against other insects, notably the codling moth though, as is characteristic with organic compounds, it is not effective against all species (Siegler and Smith, *ibid.*, 1935, **28**, 772).

Fifteen phenothiazines with different substituents like alkyl, alkoxy, and halogen were prepared with a view to studying the effect of these substituents on the insecticidal activity. These alkyl, alkoxy and halogen groups have been chosen as these substituents are known to effect a marked variation in the solubility of the compounds in lipoid and water, an important factor controlling insecticidal activity.

The substituted phenothiazines were prepared by fusing sulphur and substituted diphenylamines in the presence of 1.2 moles of anhydrous aluminium chloride (Ackermann, Friedländer, 1911, X, p. 144). The diphenylamines required in the above experiment were obtained by condensing acetylated aromatic amines, viz., 2-methoxy-, 4-methoxy-, 2-ethoxy-, 2-chloro- and 4-chloro-aminobenzenes with bromobenzene, ethylbromobenzene and *para*-bromotoluene in presence of freshly precipitated copper, using nitrobenzene as the solvent after the method of Goldberg (*Ber.*, 1907, **40**, 4543) and subsequent deacetylation with dilute hydrochloric acid and ethanol.

Experimental

Substituted Diphenylamines.—The appropriate acetanilide (1 *M*) fused potassium carbonate (2 g.), bromobenzene (1 *M*) and a trace of freshly precipitated copper were taken in nitrobenzene (15 c.c.) and slowly refluxed for 15 hours. The nitrobenzene was steam-distilled and the residue was taken up in ether. The ethereal extract was dried over anhydrous sodium sulphate. After removal of the ether the acetyldiphenylamine was refluxed with ethanol and HCl (conc.) and made alkaline with caustic soda solution when the substituted diphenylamine was obtained as a dark-coloured solid, which was crystallised from ethanol. The m.p., yield and percentage of nitrogen are recorded in Table I.

TABLE I

Diphenylamines.	M.P	% Yield.	Formula.	% Nitrogen. Found.	Calc.
2-Methoxy-	71°	80.0	$C_{13}H_{13}NO$	6.91	7 04
4-Methoxy-	79°	85 5	$C_{13}H_{13}NO$	6.85	7.04
4-Ethoxy-	61°	75.5	$C_{14}H_{15}NO$	6.10	6 50
2-Chloro-	65°	80.2	$C_{12}H_{10}NCl$	6.10	6.80
4-Chloro-	61°	80.2	$C_{12}H_{10}NCl$	6.00	6.80
2-Methoxy-4'-methyl-	50°	75 5	$C_{14}H_{15}NO$	6 10	6.60
4-Methoxy-4'-methyl-	55°	75.2	$C_{14}H_{15}NO$	6.15	6.60
4-Ethoxy-4'-methyl-	69°	81.5	$C_{15}H_{17}NO$	5 98	6.14
2-Chloro-4'-methyl-	80°	81.5	$C_{13}H_{12}NCl$	6.10	6.40
4-Chloro-4'-methyl-	85°	86 0	$C_{13}H_{12}NCl$	6.00	6.40
2-Methoxy-4'-ethyl	56°	74.9	$C_{15}H_{17}NO$	6.02	6 16
4-Methoxy-4'-ethyl-	58°	79.0	$C_{15}H_{17}NO$	5.98	6.16
4-Ethoxy-4'-ethyl-	59°	69.0	$C_{16}H_{19}NO$	5.24	5 81
2-Chloro-4'-ethyl-	70°	65.4	$C_{14}H_{14}NCl$	5 95	6.08
4-Chloro-4'-ethyl-	75°	70.4	$C_{14}H_{14}NCl$	5.88	6.08

Substituted Phenothiazines.—The phenothiazines were obtained by following the method of Ackermann (*loc. cit.*).

The appropriate diphenylamine (1 *M*), sulphur (1 *M*) and anhydrous aluminium chloride (1.2 *M*) were heated to 140-50° till the mixture had attained a molten state. When H_2S ceased to evolve, the temperature of the bath was raised to 160° and kept for half an hour at that temperature. The melt was washed several times with hot water and the residue was dissolved in ethanol and dried over anhydrous sodium sulphate. On removal of the ethanol, solid phenothiazine separated out. It was crystallised from ethanol. The m.p., yield and percentages of sulphur are recorded in Table II.

TABLE II

Phenothiazines.	M.P.	% Yield.	Formula.	% Sulphur. Found.	Calc.
1-Methoxy-	190°	70.0	$C_{13}H_{11}NSO$	13.63	13.97
3-Methoxy-	200°	75.2	$C_{13}H_{11}NSO$	13 57	13.97
3-Ethoxy-	180°	82.4	$C_{14}H_{13}NSO$	12.76	13.17
1-Chloro-	175°	79.5	$C_{12}H_8NSCl$	13.42	13.71
3-Chloro-	188°	74.5	$C_{12}H_8NSCl$	13.34	13.71
1-Methoxy-7 methyl-	200°	70 1	$C_{14}H_{13}NSO$	12.84	13.61
3-Methoxy-7-methyl-	210°	75.4	$C_{14}H_{13}NSO$	12.62	13.61
3-Ethoxy-7-methyl-	190°	70.3	$C_{15}H_{15}NSO$	12 24	12.45
1-Chloro-7-methyl-	185°	70.0	$C_{13}H_{10}NSCl$	12 78	12.92
3-Chloro-7-methyl-	190°	75.0	$C_{13}H_{10}NSCl$	12 36	12.92
1-Methoxy-7-ethyl-	205°	74 0	$C_{15}H_{15}NSO$	11.96	12.45
3-Methoxy 7-ethyl-	220°	65.0	$C_{16}H_{15}NSO$	12.14	12.45
3-Ethoxy-7-ethyl-	195°	70.3	$C_{16}H_{17}NSO$	11.52	11.81
1-Chloro-7-ethyl-	198°	78.0	$C_{14}H_{12}NSCl$	12.08	12.24
3-Chloro-7-ethyl-	200°	75.8	$C_{14}H_{12}NSCl$	11.86	12.24

CHEMICAL LABORATORIES,
UNIVERSITY OF LUCKNOW,
LUCKNOW.

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POTENTIOMETRIC STUDIES ON THE REACTION BETWEEN MERCUROUS (MERCURY) AND POTASSIUM FERRICYANIDE

By Ram Sahai Saxena

The reaction between mercurous nitrate and potassium ferricyanide has been studied potentiometrically, using Hg^{2+}/Hg_2^{2+} electrode. The equivalence point obtained from the maximum $\Delta E/\Delta C$ corresponds to the formation and precipitation of the compound $(Hg_2)_3[Fe(CN)_6]_2$, both in the case of the direct and the inverse titrations. The titration curves have a regular form: there is a good break in potential at the equivalence point and the results are accurate and reproducible. The effect of alcohol on the end-point and on the nature of curves has been studied. The results of potentiometric titrations are in conformity with the conclusions of Saxena and Bhargav, obtained by conductance measurements.

There is hardly any reference in literature to the study of this reaction by physico-chemical methods. Whereas the reaction between $Hg_2(NO_3)_2$ and $K_4Fe(CN)_6$ has already been studied potentiometrically by Saxena and Bhatnagar (this *Journal*, 1954, **31**, 157) and that between $Hg_2(NO_3)_2$ and $K_3Fe(CN)_6$ by conductivity measurements by Saxena and Bhargav (*Z. anorg. allg. Chem.*, 1954, **276**, 204), the present paper incorporates the study of the latter reaction by potentiometric method.

Experimental

Merck's guaranteed extra pure reagents were used. The solutions of mercurous nitrate and potassium ferricyanide were standardised as described earlier (*loc. cit.*). Using different concentrations of the reactants, the potentiometric titrations were performed by the direct and the inverse methods, *i.e.* when $Hg_2(NO_3)_2$ solution from the microburette was added to $K_3Fe(CN)_6$ solution in the electrode vessel and *vice versa*. In either case, mercurous nitrate containing mercuric nitrate (1%) was used to make Hg^{2+}/Hg_2^{2+} electrode. A foil of platinised platinum was immersed in the titre and used as an indicator electrode in conjunction with a saturated calomel electrode by means of a KNO_3 bridge. E.M.F. was measured on a Cambridge p_H meter. Curves were plotted (not shown) between the volume of the titrant and the E observed. The equivalence point was calculated from the maximum value of $\Delta E/\Delta C$ in each case. Titrations were also carried out in presence of alcohol up to a total concentration of 20% by volume; 20 c.c. of the solution was taken in the cell each time.

Table I

Summary of results of potentiometric titrations.

$Hg_2(NO_3)_2$ or $K_3Fe(CN)_6$ required (in c.c.) for formation of $(Hg_2)_3[Fe(CN)_6]_2$.

$Hg_2(NO_3)_2$ soln.	K_3FeCy_6 soln.	Calc.	Obtained from $\Delta E/\Delta C$ in presence of alcohol 0%.	10%.	20%.	$Hg_2(NO_3)_2$ soln.	K_3FeCy_6 soln.	Calc.	Obtained from $\Delta E/\Delta C$ in presence of alcohol 0%.	10%.	20%.
			Direct titrations.						Inverse titrations.		
0.26*M*	0.05*M*	5.77	5.45	5.55	5.70	*M*/20	*M*/7.0	4.66	4.54	4.60	4.65
M/10	*M*/50	6.00	5.80	5.85	5.95	*M*/60	*M*/20	4.44	4.32	4.36	4.15
M/50	*M*/300	4.99	4.90	4.95	5.00	*M*/200	*M*/75	5.00	4.95	5.00	5.00

Discussion

The potentiometric titration curves, both in the direct and the inverse titrations, yield only one break in potential corresponding to the formation and complete precipitation of the compound $(Hg_2)_3[Fe(CN)_6]_2$, where the molecular ratio of the reactants, $Hg_2(NO_3)_2$ and $K_3Fe(CN)_6$, is 3 : 2. The formation of the intermediate compound $KHg_2Fe(CN)_6$, as suggested by the results of conductometric titration (*loc. cit.*), has not been indicated by the potentiometric results.

It is clear from Table I that the observed points of equivalence (obtained from max. $\Delta E/\Delta C$) in aqueous medium are slightly lower than those calculated for the formation of $(Hg_2)_3[Fe(CN)_6]_2$ and by the addition of alcohol in increasing amounts, the observed titre values gradually approach the calculated points of equivalence.

The discrepancy between the observed and the calculated titre values in aqueous medium and the subsequent change, when the titrations are performed in alcoholic medium, support our views on the adsorptive behaviour of such ferro- and ferricyanide complexes (cf. R. S. Saxena and co-workers, previous publications). The effect of adsorption of Hg_2^{2+} and $Fe(CN)_6^{3-}$ ions from the surrounding solution by the precipitated compound would be to decrease the titre values in aqueous medium in both cases which should then increase in presence of alcohol, which helps to check adsorption. This has actually been observed. The effect of adsorption is more marked in concentrated solutions than in dilute solutions.

In all titrations a brownish yellow precipitate is formed and the supernatant liquid is marked by a sharp change to a light greenish tinge just before the end-point. In direct titrations, the potential is stable from the beginning but changes greatly on each addition of mercurous nitrate, a little before the end-point, and it takes about half an hour after each addition for the potential to become steady. After the equivalence point is crossed, the potential changes in a regular manner. In the inverse titrations, however, the potential remains steady throughout. It first decreases, then begins to increase just before the end-point, which is then marked by a sharp jump. The latter titrations take a shorter time than the former. The presence of alcohol decreases the break in potential at the equivalence point in either case. The titrations give accurate and reproducible results

From the potentiometric titrations, it can be concluded that the composition of mercurous ferricyanide is expressed by the formula $(Hg_2)_3[Fe(CN)_6]_2$, which is in fair agreement with the results obtained from conductivity (*loc. cit.*).

Chemical Laboratories,
Government College,
Kota (Rajasthan).

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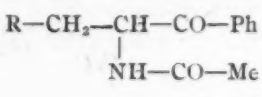
*iso*QUINOLINE DERIVATIVES. PART III

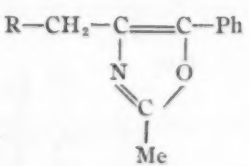
By T. N. Ghosh, Bhabatosh Bhattacharya and Saktipada Datta

In contrast with the earlier observation (Ghosh and Dutta, this *Journal*, 1955, **32**, 17, 755) that treatment of (α-acetamido-β-phenyl)-ethylmethyl ketone and of β-phenyl-substituted analogues with $POCl_3$ or conc. H_2SO_4 leads to the formation of 1-methyl*iso*quinoline derivatives, accompanied with dehydrogenation and deacetylation, (α-acetamido-β-phenyl)-ethylphenyl ketone and β-phenyl-substituted analogues yield, under similar condition oxazole derivatives Methyl α-acetamido-α-methyl-β-phenylpropionate undergoes the Bischler-Napieralski cyclisation to yield the corresponding *iso*quinoline derivative. Condensation of α-acetamido-α-methyl-β-phenylpropionyl chloride with ethyl sodiomalonate leads to the formation of an oxazole derivative.

It has been shown (Ghosh and Dutta, this *Journal*, 1955, **32**, 17, 755) that treatment of (α-acetamido-β-phenyl)-ethylmethyl ketone with phosphorus oxychloride leads to the formation of 1-methyl*iso*quinoline, the process involving cyclodehydration, dehydrogenation and deacetylation. The reaction can be effected by concentrated sulphuric acid as well and can be applied to β-phenyl-substituted analogues. However, it has been stated that the exact sequence of the three processes involved is not clear. In order to get an insight into the exact mechanism of the reaction, it is thought desirable to prepare analogous α-acylamidoketones with various substitutions and subject them to the action of such reagents as phosphorus oxychloride or concentrated sulphuric acid. Accordingly, α-acetamido-β-phenylpropionic acid and the corresponding *o*-chloro- and *p*-chloro-phenyl analogues have been subjected to the Dakin and West reaction (*J. Biol. Chem.*, 1928, **78**, 91, 745, 757) with benzoic anhydride in presence of pyridine to obtain the corresponding ketone (I). When treated with phosphorus oxychloride, (I) undergoes cyclisation with the formation of a non-basic compound, which is evidently represented by the oxazole structure (II) (cf. Wiley, *J. Org. Chem.*, 1947, **12**, 43).

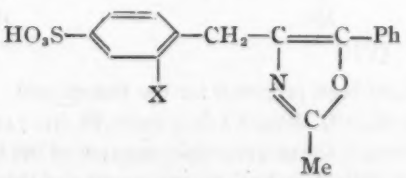


(I)



(II)

[R = Ph, *o*-Cl.C_6H_4, *p*-Cl.C_6H_4]

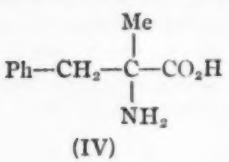


[III : X = H or Cl]

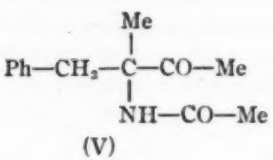
The significant point that emerges from the above observation is that the acylamidoketone, R_1-CH_2.CH(NH.CO.CH_3)-CO-R_2 (R_1 = Ph ; R_2 = Me or Ph), is capable of furnishing under the influence of a cyclising agent such as phosphorus oxychloride or concentrated sulphuric acid, either an *iso*quinoline or an oxazole derivative, depending on the nature of R_2. When R_2 is methyl, an *iso*quinoline is obtained, the process involving deacetylation and dehydrogenation also (Ghosh and Dutta, *loc. cit.*[1]). On the other hand, an oxazole of the type (II) is obtained under the same condition, when R_2 is phenyl.

Treatment of (I : R = Ph or *o*-Cl.C_6H_4) with concentrated sulphuric acid affords a mono-sulphonic acid derivative of (II), also obtained by subjecting (II) to similar action of concentrated sulphuric acid. When, however, (I : R = *p*-Cl.C_6H_4) is similarly treated with concentrated sulphuric acid, (II : R = *p*-Cl.C_6H_4) is obtained without any formation of the corresponding sulphonic acid derivative. It may therefore be reasonably argued that in the former cases the sulphonic acid group occupies the *para*-position of the phenyl nucleus, as shown in the formulation (III).

It was considered worthwhile at this stage to prepare some α-acylamidoketones having a quaternary carbon atom in the α-position so that the possibllity of an oxazole formation may be avoided, but having configuration suitable for *iso*quinoline formation. The preparation of the ketone (V), embracing such features, was attempted. The attractive route to (V) appeared to be the preparation of the amino-acid (IV), so that by the Dakin and West reaction (IV) could possibly be converted into (V) with acetic anhydride in presence of pyridine. Hydrolysis of 5-benzyl-5-methylhydantoin (Bucherer and Lieb, *J. prakt. Chem.*, 1934, **141**, 5) with alkali has now readily furnished the amino-acid (IV). When, however, (IV) is treated with acetic anhydride in presence of pyridine, the corresponding acetamido derivative (VI) is obtained, to the exclusion of any ketone. Even the use of acetyl chloride did not result in the Dakin and West reaction in this particular case.



(IV)



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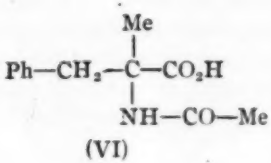
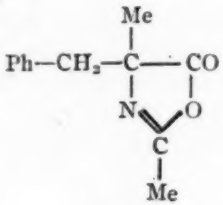
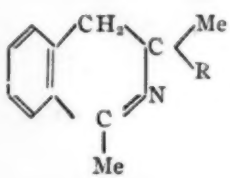


(VI)



(VII)



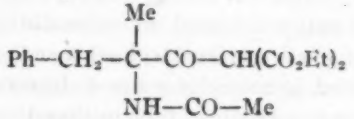
(VIII)

Two mechanisms have been proposed for the Dakin and West reaction. The one proposed by Dakin and West (*J. Biol. Chem.*, 1928, **78**, 91, 745, 757) involves acetylatiou of the amino-acid, cyclisation to the azlactone, reaction of the latter compound with base to afford a resonance-stabilised carbanion, the reaction of this ion with acetic anhydride

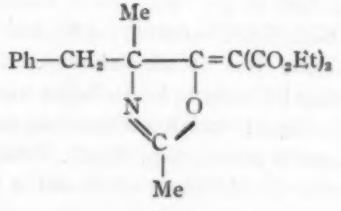
to provide the azlactone with an α-acetamido-β-keto acid and acetate ion, and the subsequent conversion of this azlactone into the acetamidoketone and carbon dioxide. This view is supported by Attenburrow *et al.* (*J. Chem. Soc.*, 1948, 310), Cleland and Niemann (*J. Amer. Chem. Soc.*, 1949, **71**, 841) and Cornforth and Elliott (*Science*, 1950, **112**, 534), and it is considered that only those α-amino-acids or their derivatives, which are capable of forming azlactones containing an active α-hydrogen atom, will undergo the Dakin and West reaction. Wiley (*Science*, 1950, **111**, 259), however, rejects this mechanism in favour of an initial base-catalysed decarboxylation, the carbanion then reacting with the acetic anhydride or other carbonyl component to give rise to the corresponding ketone. The observation, now made, that the amino-acid (IV) does not respond to the Dakin and West reaction can, however, be explained on the basis of the azlactone mechanism, for no hydrogen atom replaceable by acetyl, is available in the azlactone (VII), which is capable of formation from (IV) *via* (VI). This observation, however, cannot be accommodated in Wiley's mechanism, as (VI) could provide a carbanion by decarboxylation.

It is noteworthy that the methyl ester of (VI), on cyclodehydration with $POCl_3$, readily furnishes 1 : 3-dimethyl-3-carbomethoxy-3 : 4-dihydro*iso*quinoline (VIII : R = CO_2Me) as a reddish gummy mass, characterised as picrate. This was hydrolysed by 20% caustic soda solution to the acid (VIII : R = CO_2H).

An alternative route to (V), involving condensation of ethyl sodiomalonate with the acid chloride of (VI), results in the formation of a compound which is, however, devoid of ketonic property, does not exhibit any ferric reaction, and is slowly hydrolysed at room temperature by 5% aqueous caustic soda to the acid (VI). These properties and the analytical figures are in accord with the structure (X), evidently obtained from (IX), initially formed. The next attempt consisted in condensation of ethyl α-acetamido-α-methyl-β-phenylpropionate, in toluene medium, with ethyl acetate in presence of anhydrous sodium ethoxide, and yielded a deep red liquid on acidification. This liquid, which develops a positive ferric reaction, has furnished, when heated with 15% hydrochloric acid a resin-like substance which is found to be an acid, devoid of ketonic property. It decolorises bromine water. However, attempts to purify and crystallise the substance have failed.



(IX)



(X)

The above observations suggest that it may be advantageous to prepare the *N*-phthalimido derivative of the amino-acid (IV) and then to effect the condensation of the ethyl ester of the phthalimido derivative with ethyl acetate under the Claisen condition. However, it was not found possible to induce (IV) to condense with phthalic

anhydride under conditions which Vanags and Veinbergs (*Ber*, 1942, **75B**, 1558) successfully employed in the case of a number of amines and amino-acids. Whether steric hindrance is at play in the present case due to the adjacent quaternary carbon atom is difficult to say. However, work is in progress along other directions to gain an insight into the manner in which deacetylation and dehydrogenation take place in the formation of *iso*quinoline derivatives, as mentioned at the outset.

EXPERIMENTAL

α-Carboxy-α-acetamido-β-phenylpropionic Acid.—Ethyl α-carbethoxy-α-acetamido-β-phenylpropionate (Albertson and Archer, *J. Amer. Chem. Soc.*, 1945, **67**, 308) (6.8 g.) was treated with NaOH (2.7 g.) in water (27 c.c.) and refluxed on a steam-bath for about 5 hours. The clear solution was just acidified with HCl (conc.) and the precipitated solid crystallised from aqueous ethanol (charcoal) in colorless rectangular plates (5.2 g.), m.p. 145-46° (decomp.). (Found : N, 5.34. $C_{12}H_{13}O_5N$ requires N, 5.57%).

α-Acetamido-β-phenylpropionic Acid.—A mixture of the above dibasic acid (5.2 g.) and water (17 c.c.) was heated under reflux for about 4 hours till CO_2 had ceased to evlove. On cooling, a crystalline solid was obtained, which was filtered and a further quantity was recovered by concentrating the mother-liquor. The solids were crystallised from water in colorless needles (3.4 g.), m.p. 147°. (Found : N, 6.62. $C_{11}H_{13}O_3N$ requires N, 6.76%).

(*α-Acetamido-β- phenyl*)-*ethylphenyl Ketone* (I : R = Ph).—A mixture of α-acetamido-β-phenylpropionic acid (10 g.), benzoic anhydride (24 g.) and pyridine (24 g.) was heated on a steam-bath for 6 hours. The mixture after steam-distillation deposited a solid on cooling which was filtered, thoroughly triturated with 5% aqueous sodium bicarbonate solution and then crystallised from ethanol in colorless needles (9 g.), m.p. 107-108°. (Found : N, 5.46. $C_{17}H_{17}O_2N$ requires N, 5.24%).

The 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol in yellow needles, m.p. 227-28°. (Found : N, 15.58. $C_{23}H_{21}O_5N_5$ requires N, 15.66%).

2-*Methyl*-4-*benzyl*-5-*phenyloxazole* (II : R = Ph).—A mixture of the above compound (I : R = Ph) (7 g.), nitrobenzene (50 c.c.) and $POCl_3$ (7 c. c.) was heated under reflux in an oil-bath at 170°-180° for 8 hours. The mixture was cooled, treated with water and then with NaOH solution (15%, 50 c.c.) and finally subjected to steam-distillation till practically free of nitrobenzene. The residue was extracted with ether and removal of the ether left a dark, heavy liquid which distilled at 220-25°/6-7 mm to furnish a brown, mobile liquid which solidified on standing and crystallised from methanol in colorless rectangular plates, m.p. 68-69°. (Found : N, 5.74. $C_{17}H_{15}ON$ requires N, 5.62%). It is insoluble in cold dilute alkali and in HCl (conc.).

Treatment of (I : R = Ph) *with* H_2SO : *Formation of the Sulphonic Acid* (III : X = H).—A solution of (I : R = Ph) (6 g.) in H_2SO_4 (conc., 20 c.c.) was allowed to stand at room temperature for 1 hour and then heated on the steam-bath for 1 hour. The cooled solution was poured into water, when a pasty mass was deposited, which turned granular when allowed to stand overnight. The acidic solution did not furnish any product on basification with NaOH.

The solid, readily soluble in aqueous sodium bicarbonate but insoluble in HCl, was crystallised from water (charcoal) in colorless plates (3.8 g.), m.p. 328-30° (decomp.). (Found : N, 4.38 ; S, 10.15 ; chem. equiv., 332. $C_{17}H_{15}O_4NS$ requires N, 4.25 ; S, 9.72%; chem. equiv., 329).

The above sulphonic acid was also obtained by treatment of (II : R= Ph) with concentrated sulphuric acid under identical condition.

(α-*Acetamido-β-o- chlorophenyl*) - *ethylphenyl Ketone* (I : R= *o*-Cl.C_6H_4).—The method of preparation was the same as in the case of (I : R=Ph). α-Acetamido-*β-o*-chlorophenylpropionic acid used was prepared according to the method previously recorded (Ghosh and Dutta, this *Journal*, 1955, **32**, 755). The ketone was crystallised from aqueous ethanol in colorless rectangular plates, m.p. 105-106°. (Found : N, 4.81. $C_{17}H_{16}O_2NCl$ requires N, 4.64%).

The 2 :4-*dinitrophenylhydrazone* crystallised from ethanol in yellow needles, m.p. 200°. (Found : N, 14.26. $C_{23}H_{20}O_5N_5Cl$ requires N, 14.53%).

2-*Methyl*-4 (*o-chloro*)-*benzyl*-5-*phenyloxazole* (II : R= *o*-Cl.C_6H_4).—Using (I : R= *o*-Cl.C_6H_4 ; 12 g.), $POCl_3$ (12 c.c.) and toluene (80 c.c.) and heating the mixture at 120-30° for 8 hours in an oil-bath, (II : R= *o*.Cl.C_6H_4) was prepared as in the previous case and was crystallised from ethanol in colorless needles (7.4 g.), m.p. 87 88°. (Found : N, 4.76. $C_{17}H_{14}ONCl$ requires N, 4.93%). It is insoluble in cold dilute alkali and in HCl (conc.)

Treatment of (I : R = *o*-Cl.C_6H_4) *with* H_2SO_4 : *Formation of the Sulphonic Acid* (III : X= Cl).—The method of procedure was the same as described previously. The product was obtained as a pasty mass which, when kept *in vacuo*, furnished a granular solid, crystallising as a colorless micro-crystalline powder (m.p. 298-300°) from benzene-ethanol mixture. (Found : N, 3.63 ; chem. equiv., 360. $C_{17}H_{14}O_4NClS$ requires N, 3.85% ; chem. equiv., 363.5).

(α-*Acetamido-β-p-chlorophenyl*)-*ethylphenyl Ketone* (I : R = *p*-Cl.C_6H_4).—The method of prepration was the same as in the case of (I : R=Ph). α-Acetamido-*β-p*-chlorophenylpropionic acid used was prepared according to the method previously recorded (Ghosh and Dutta, *loc. cit.*). The ketone was crystallised from aqueous ethanol in colorless needles, m.p. 151-52°. (Found : N, 4.72. $C_{17}H_{16}O_2NCl$ requires N, 4.64%).

The 2 :4-*dinitrophenylhydrazone* was crystallised from ethanol in yellow needles, m.p. 245-46°. (Found : N, 14.68. $C_{23}H_{20}O_5N_5Cl$ requires N, 14.53%).

Methyl-4-(p-*chloro*)-*benzyl*-5-*phenyloxazole* (II : R= *p*-Cl.C_6H_4) was prepared as in the case of (II : R= *o*-Cl.C_6H_4) and was crystallised from aqueous ethanol in colorless needles, m.p. 107-108°. (Found : N, 5.21. $C_{17}H_{14}ONCl$ requires N, 4.93%). It is insoluble in cold dilute alkali and in concentrated hydrochloric acid. The same compound (mixed m.p. 107-108°) was obtained when (I : R= *p*-Cl.C_6H_4) was treated with concentrated sulphuric acid, and no trace of any sulphonic acid was formed.

α-*Methyl*-α-*amino*-*β*-*phenylpropionic Acid* (IV).—5-Benzylhydantoin (Bucherer and Lieb, *loc. cit.*) (20.4 g.) was treated with NaOH (17.6 g.) in water (75 c.c.) and refluxed on a steam-bath for 24 hours. After treatment with Nuchar, the clear solution was acidified with HCl and filtered to remove a small quantity of impurity. The solution

was evaporated to dryness and the solid residue extracted with anhydrous ethanol. The ethanolic solution was concentrated to 75 c.c. and then treated with pyridine when the amino-acid (14 g.) was precipitated, which was crystallised from aqueous ethanol in colorless rectangular plates, m.p. 263-64°. (Found : N, 7.84. $C_{16}H_{13}O_2N$ requires N, 7.82%). It is moderately soluble in cold water, but readily soluble in hot water and in aqueous sodium bicarbonate solution.

The *acetamido* derivative (VI) was obtained, to the exclusion of any ketone, by treating the above amino-acid with acetic anhydride in presence of pyridine and was crystallised from ethanol in colorless needles, m.p. 203-204°. (Found : N, 6 36. $C_{12}H_{15}O_3N$ requires N, 6.33%). The *benzamido* derivative, similarly obtained, was crystallised from ethanol in colorless, micro-crystalline powder, m p. 204°. (Found : N, 4.82. $C_{17}H_{17}O_3N$ requires N, 4.94%).

Methyl α-Acetamido-α-methyl-β-phenylpropionate.—A solution of (VI : 29 g.) in anhydrous methanol (180 c.c.) containing H_2SO_4 (conc., 1.8 c.c.) was refluxed on the steam-bath for 6 hours. After distilling off most of the methanol, the residue was poured into water. The solid was triturated with 5% aqueous sodium bicarbonate solution, washed with water and crystallised from water in colorless plates (16 g.), m.p. 119-20°. An analytical sample was dried *in vacuo* over P_2O_5 at 90-95°. (Found : N, 5.72. $C_{13}H_{17}O_3N$ requires N, 5.95%).

1 : 3-*Dimethyl-3-carbomethoxy-3* : 4-*dihydro*isoquinoline (VIII : R= CO_2Me).— A mixture of the above methyl ester (8 g.), toluene (100 c.c.) and $POCl_3$ (8 c.c.) was heated under reflux in an oil-bath at 115-20° for 7 hours. After distilling off toluene and excess of $POCl_3$, the residue was treated with cold aqueous caustic soda solution (5%) and then washed with water. The dark mass was extracted thrice with HCl (dil.) and the acid extract, on basification with cold dilute caustic soda solution, furnished a reddish gummy mass (2.5 g). It was somewhat purified by acid-alkali treatment and gave, in benzene solution, a *picrate* which crystallised from benzene in yellow needles, m.p. 182-83°. (Found : C, 50.58 ; H, 4.32 ; N, 12.48. $C_{13}H_{15}O_2N.C_6H_3O_7N_3$ requires C, 51.12 ; H, 4.03 ; N, 12.55%).

1 : 3-*Dimethyl-3-carboxy-3* : 4 - *dihydro*isoquinoline (VIII : R= CO_2H).—A mixture of (VIII : R=CO_2Me) (1 g.) and caustic soda (20 %, 15 c.c.) was refluxed on the steam-bath for 8 hours. On dilution with water, a clear solution was obtained, which on acidification with HCl (conc.) yielded a solid (0.65 g.). It was crystallised from ethanol (charcoal) in colorless plates, m.p. 241-42°. (Found : N, 6.76. $C_{12}H_{13}O_2N$ requires N, 6.89%). It is soluble in aqueous sodium bicarbonate solution.

2 : 4-*Dimethyl-4-benzyl-5-dicarbethoxymethylene-4* : 5-*dihydroxazole* (X).—A mixture of the acid (VI : 20 g.), anhydrous benzene (100 c.c.) and thionyl chloride (14.6 g.) was gradually heated in an oil-bath and the temperature was maintained at 55-60° for 1 hour. After removal of the benzene and excess of thionyl chloride *in vacuo*, the resulting acid chloride, when thoroughly cooled, was added gradually to a stirred slurry of ethyl sodiomalonate (16.8 g.) and anhydrous benzene (100 c.c.), set aside overnight and then heated under reflux on a steam-bath for 7 hours. After filtration, benzene was removed *in vacuo*, and the residual liquid was found to distil over a wide range (120°-190°/10-12 mm) ; it furnished a colorless, heavy liquid (10.5 g.) which solidified on

scratching. The solid was crystallised thrice from petroleum ether (b.p. 60°-80°) in colorless needles, m.p. 97-98°. (Found : C, 66.32 ; H, 7.21. $C_{19}H_{23}O_5N$ requires C, 66.08 ; H, 6.67%).

When the above compound (X) was stirred with aqueous NaOH solution (5%) at room temperature, gradually a clear solution was obtained, which on acidification with concentrated hydrochloric acid furnished a solid. After crystallisation from ethanol, it was identified as (VI).

Ethyl α-acetamido-α-methyl-β-phenylpropionate was similarly prepared as the methyl ester and was crystallised from aqueous ethanol in colorless rectangular plates, m.p. 101-102°. (Found : N, 5.34. $C_{14}H_{19}O_3N$ requires N, 5.62%).

The authors are grateful to Dr. U. P. Basu, Director of the Institute, for his continued interest.

BENGAL IMMUNITY RESEARCH INSTITUTE,
CALCUTTA-16.

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SHORT NOTES

MERCAPTAN AS A CHAIN-TRANSFER AGENT IN EMULSION POLYMERISATION OF STYRENE

By P. R. Sinha and K. L. Mallik

Although mercaptan is being used in emulsion polymerisation of butadiene-styrene on a large scale at low temperatures, not much work has been done on the kinetics of mercaptan reaction at such temperatures. Kolthoff, Meehan and Sinha (*J. Polymer Sci.*, 1955 **16**, 471) determined the chain-transfer constants of primary and tertiary mercaptans in emulsion polymerisation of styrene and butadiene at 5° and found the values slightly higher than the corresponding values at 50°. For low temperature work, they used a redox initiator, as commonly used. Kharash, Nudenberg and Kwahara (*J. Org. Chem.*, 1955, **20**, 1550) suggested that at low temperatures, the mercaptan reacted with ferric ions, produced from the redox reaction, and not with the growing polymer radicals, and the resulting mercaptide radical terminated the growing polymer chain instead of reacting with the monomer to start another chain. Thus, the modification by mercaptan at low temperatures proceeds through the mechanism of chain termination instead of chain transfer, which is the accepted mechanism. The object of the present work has been to examine the above suggestion.

As the mechanism of initiation by redox systems, especially the organic hydroperoxides and ferrous salts, is complicated and subject to controversy, it is desirable to use an initiator, the mechanism of which is simple; potassium persulphate is eminently suitable from that consideration. But the thermal decomposition of potassium persulphate at low temperature is so low that it has not been used before. To counteract partially the effect of low temperature, a concentrated solution (almost saturated) of potassium persulphate has been used in the present investigation.

The recipe used (in parts) was styrene 100, water 180, potassium myristate 5, potassium persulphate 3.2, *n*-octylmercaptan 0.5-1.0.

Styrene was first treated with caustic soda solution, washed, dried and distilled twice at 40° under nitrogen atmosphere. Potassium myristate was prepared from myristic acid and crystallised thrice from alcohol and dried *in vacuo* at room temperature. Potassium persulphate (Merck, G. R) was crystallised from water. *n*-Octylmercaptan (Olin Mathison) was fractionally distilled at low pressure and the fraction at 40-42° was collected; the sulphur content was found as 21.8% against the theoretical value of 21.9%. Experiments were done in Jena bottles with rubber gaskets and nitrogen atmopshere was maintained in the system. Bottles were rotated at 40 r.p.m. inside the bath, kept at a temperature of 5°±1°. Samples were withdrawn from the bottle with a hypodermic syringe; for determination of conversion, samples were injected into alcohol containing quinhydrone, wherein the polymer was coagulated; it was filtered, washed with alcohol and dried at 100° and weighed. For mercaptan analysis, samples were injected into

100 c.c. of alcohol containing sufficient ferrous sulphate to decompose persulphate ; excess ammonia was added and the mercaptan was amperometrically titrated with standard silver nitrate solution (Kolthoff and Harris, *Ind. Eng. Chem. Anal. Ed.*, 1946, **18**, 161). The chain-transfer constant (*C*) was calculated with the formula of Mayo,

$$\frac{d \ln(RSH)}{d \ln(M)} = C$$

where RSH designates the mercaptan and M, the monomer.

The rate of polymerisation was found to be 2.1% per hour and it was the same in absence of mercaptan in the above recipe. This is expected from the mechanism of chain transfer. *C* was found as 19.3; the value found by Kolthoff *et al.* (*loc. cit.*) was 23 with redox initiator. The difference may be due to some reaction of mercaptan with the redox initiator. The thermal decomposition of persulphate is so low that it cannot account for even a very small fraction of disappearance of mercaptan. There is not the slightest doubt about chain-transfer mechanism of mercaptan at 50° with persulphate as initiator ; the identical value of the chain-transfer constant with the same initiator at 5° definitely proves the same mechanism of mercaptan at that temperature.

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PHYSICAL CHEMISTRY LABORATORY,
JADAVPUR UNIVERSITY,
CALCUTTA.

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ON THE PREPARATION OF 4-METHYLCINNOLINE

BY A. B. LAL

The synthesis of 4-methylcinnoline has been described in the literature (Jacobs *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 1310 ; Simpson and Atkinson, *J. Chem. Soc.*, 1947, 808). In connection with another work, larger quantities of this substance were required. Attempts to prepare it by the methods already described resulted in small yields. Jacobs' method (*loc. cit.*) of dehydrating the tertiary alcohol (*o*-aminophenyldimethyl carbinol) with iodine in boiling toluene did not prove successful. The preparation of the tertiary alcohol and its subsequent dehydration, however, proceeded smoothly according to the method described by Simpson *et al.* (*loc. cit.*). The latter authors, however, diazotised and cyclised the crude *o-iso*propenylaniline to 4-methylcinnoline. Attempt to repeat this furnished a deep green residue (as described by Simpson *et al.*, *loc. cit.*) but on extracting it with petroleum ether only a red oil was obtained, which could be crystallised with difficulty, affording a small quantity of 4-methylcinnoline. When this oil was distilled under reduced pressure, 4-methylcinnoline was obtained in a low yield (b.p 146-50°/10 mm).

It was therefore concluded that the purification of the *o-iso*propenylaniline was neccessary, and accordingly the crude product was distilled (b.p. 115-20°/20 mm ; Jacobs *et al.*, *loc. cit.*, b.p. 83.5° to 87.5°/1-2 mm). This was characterised by its hydrochloride, m.p. 171-72° (Jacobs *et al.*, *loc. cit.*, record m.p. 163-68.5°) and picrate, m.p. 149-50° (flat needles from alcohol).

The pure *o-iso*propenylaniline (23 g.) was dissolved in hydrochloric acid (200 c.c., 2*N*) and concentrated hydrochloric acid (40 c.c.) was then added. A small amount of undissolved oil floating on the surface was extracted with ether (100 c.c.). The solution was cooled to 2° and sodium nitrite (11 g.) added slowly (2 hours) with stirring. The green solution, thus obtained, was again extracted with ether (100 c.c.) to remove a small quantity of a red oil. The solution was then heated up to 60° (the colour changed to red) and allowed to stand for two days at room temperature. It was neutralised with sodium carbonate (slight excess) and the yellow oil liberated was extracted with ether (thrice, 100 c.c. each), dried (anhydrous sodium carbonate) and the ether removed. This gave a brown oil which crystallised into rosettes on cooling (10.5 g.). A further quantity of green oil separated (from the solution, which had been neutralised with sodium carbonate) on addition of a concentrated solution of NaOH. This was also worked up as above and furnished light green rosettes (11 g.). Total yield 86%. Crystallisation from petroleum ether (60°-80°, charcoal) furnished yellowish white needles, m.p. 73-74° in 17.5 g. yield (75%). (Jacobs *et al.*, 72.5-74° and Simpson *et al.*, 74-75°).

Department of Chemistry
Patna University,
Patna-6.

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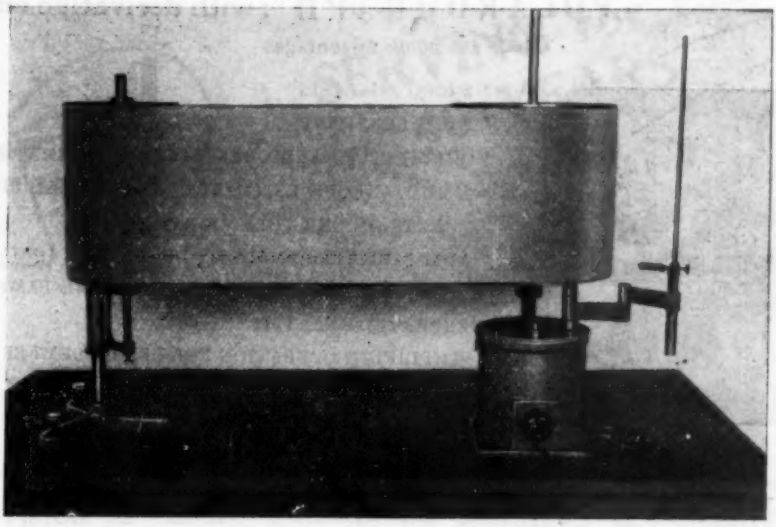

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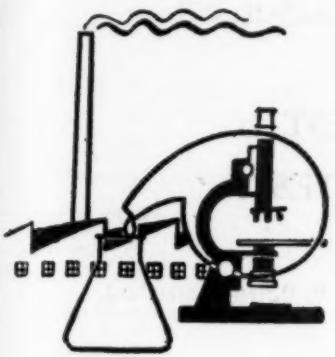

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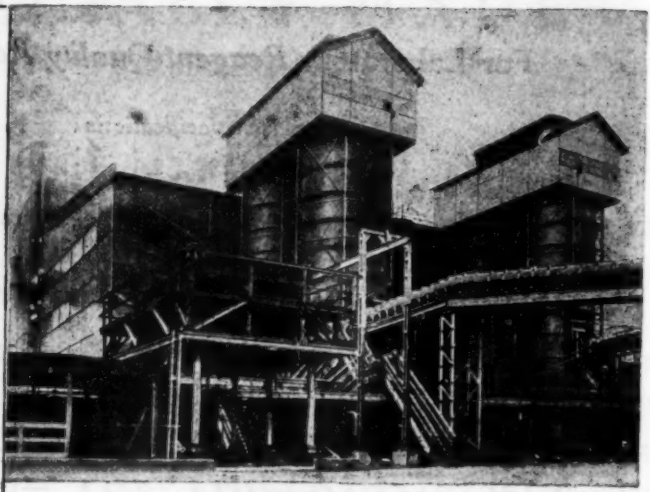

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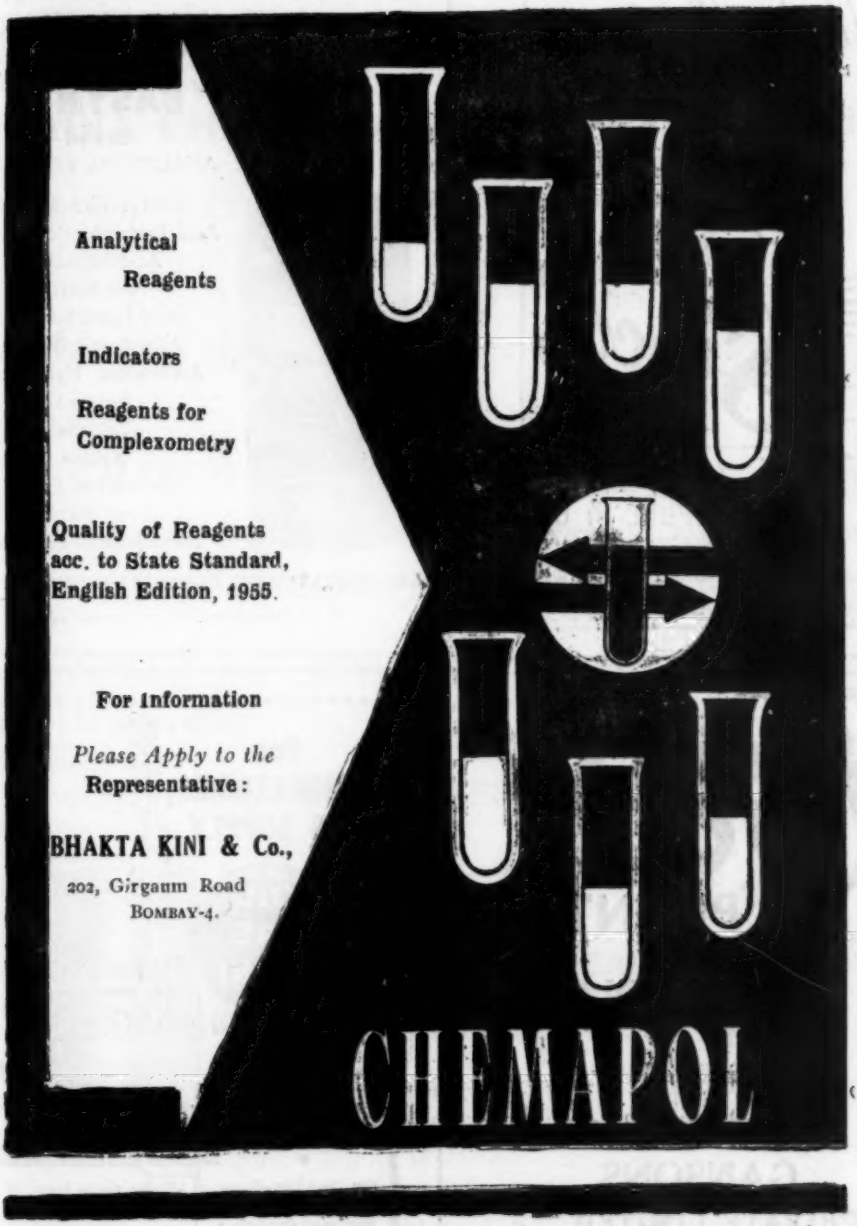

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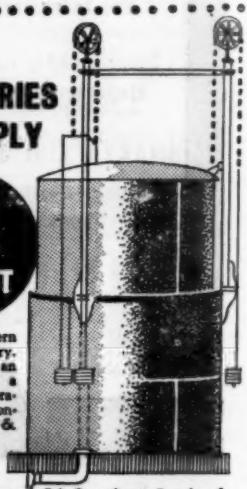

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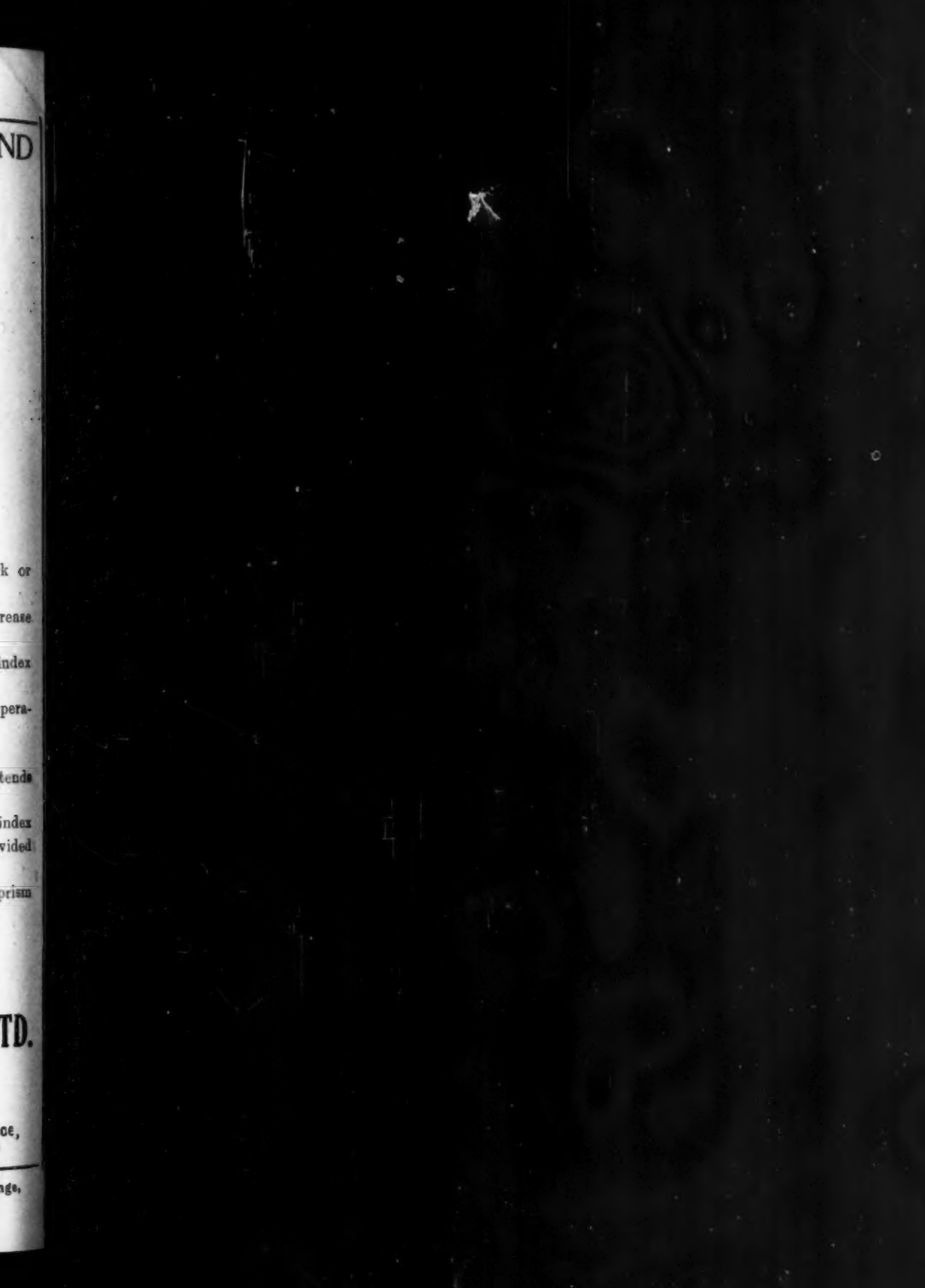
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